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**PROGRESS
REPORT**

**DEVELOPMENT OF LOW TEMPERATURE
DIELECTRIC COATINGS FOR
ELECTRICAL CONDUCTORS**

9th QUARTERLY REPORT

BY
K.N. MATHES

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Ninth Quarterly Report

October 15, 1963

DEVELOPMENT OF LOW TEMPERATURE COATING

for

ELECTRICAL CONDUCTORS

INTRODUCTION

With the extension of the subject contract for another year, emphasis will be placed on the development of multiple wire structures with optimum properties at cryogenic temperature. Designs for a number of round and ribbon constructions have been developed and arrangements made for manufacture of samples.

The more fundamental studies on cryogenic liquids in which cable or other devices may be immersed is being continued also.

This report also contains a more detailed report on European activities concerned with cryogenic liquids and nonmetallic materials at cryogenic temperatures.

SUMMARY AND CONCLUSIONS

Multiple Wire Development

Until samples of the multiple wire cables have been received and tested, no conclusions of course are possible. It is appropriate to note that an attempt will be made to utilize thin resin film coatings as the principle cable dielectric. Such an approach is counter to present generally accepted practice but particularly for cryogenic applications the attempt, though ambitious, seems well worthwhile. Moreover, other insulations are also included as back-up in case the film coating alone does not prove adequate.

Evaluation of Cryogenic Liquids

The true value of the equipment for refluxing cryogenic liquids to be used for voltage breakdown measurements must be determined by trial. It is apparent, however, from the report on the European visits that efforts to obtain very pure liquid are needed to establish bench marks against which the available breakdown values for impure cryogenic liquids can be compared.

European Report

The information obtained in Europe has been supplemented by reference to the work of American investigators in those cases where comment was made by Europeans on the American work. It is interesting and perhaps a little tragic that the Europeans quite often seem to know more about American work than is common here in the United States. No doubt the European report would be more useful if even more reference could be made to work in progress in the United States.

Perhaps the most comprehensive cryogenic work in Europe pertinent to the subject contract lies in the area of cryogenic liquids. The particularly extensive work on ionic mobility aids in understanding the voltage breakdown and AC loss measurements made in the subject work on nitrogen and helium. It is unfortunate that no similar fundamental work has been undertaken with hydrogen. The studies of intrinsic breakdown strength in cryogenic liquids and the many factors involved has direct bearing, of course, on the AC breakdown voltage measurements made under the contract on helium and nitrogen. Again, it is both surprising and unfortunate that the voltage breakdown of hydrogen seems not to have been studied anywhere except in connection with the subject contract.

The remainder of the European report provides information which is of considerable correlary value but makes no direct contribution to work under the contract.

Investigational Program

Multiple Wire Development

Two types of multiple conductors are being developed -- bundled round wire and parallel conductor ribbon cable. The production of bundled round wire samples has been sub-contracted to the G-E Wire and Cable Department at Lowell, Massachusetts. With the cooperation of P.O. Nicodemus and H. Wilson at Lowell in joint conference, the 11 samples described in Table I were developed and are in the progress of manufacture. These #16-19 strand cables will be supplemented with #26-7 strand cable which will be designed with an optimum insulation based on the results with the #16 wire.

The first three samples in Table I involve a ML resin film coating on each wire. In samples 1 and 2 the ML itself constitutes the primary insulation and the outside jacket is really only a mechanical protective. It is recognized that insulation on each strand complicates the problem of removing insulation at joints. It is expected that this problem can be solved by dipping the wire in a eutectic of NaOH and KOH which will remove the ML coating. The individual ML coated strands can also be tested electrically one to another so that in effect a bundled multiple cable is evaluated. This evaluation will be made on long lengths before other test so as to determine the reliability of ML as a primary cable insulation. If successful, tremendous space saving as well as excellent cryogenic performance should be achieved. Nevertheless, in sample 3 the ML coating has been "backed up" by a Teflon extrusion.

Samples 4, 5 and 6 make use of unbonded polyimide film (DuPont H Film) as the primary insulation with several types of mechanical armor. Samples of .001 inch H film have been obtained from the DuPont Film Department through the courtesy of R. Stabler and forwarded to Lowell.

Table I
Round Wire Samples

<u>Sample</u>	<u>Conductor*</u>	<u>Insulation</u>	<u>Shield</u>	<u>Jacket</u>
1.	#16 19/.0113 HML	Felted Asb. + ML	.005% Silver Ctd. Copper (80-90% Coverage)	-
2.	"	Glass Braid + ML	"	-
3.	"	Extruded TFE .009" Wall	"	-
4.	#16 19/.0113 Silver Ctd. Copper	"H" Film .001" x $\frac{1}{4}$ " - $\frac{1}{2}$ lap Felted Asb. + ML	"	-
5.	"	"H" Film .001" x $\frac{1}{4}$ " - $\frac{1}{2}$ lap Glass Brd. + ML	"	-
6.	"	"H" Film .001" x $\frac{1}{4}$ " - $\frac{1}{2}$ lap HT-1 Braid	"	-
7.	"	"H" Film .001" x $\frac{1}{4}$ " - $\frac{1}{2}$ lap Dacron Braid	"	-
8.	"	Extruded TFE .009" Wall	"	-
9.	"	Extruded TFE .009" Wall	"	HT-1 or Dacron Braid
10.	"	Extruded TFE .009" Wall	"	TFE Tape (Fused)
11.	"	G-E TFE .009" Wall	"	None

* #26 7/.0063 will be made also with the best insulation systems based upon the performance of the above.

Samples 8, 9 and 10 have been designed with Teflon to provide comparison with a standard material and also to evaluate jacket insulations applied over the outer braided shield. The final sample is designed to evaluate an improved type of Teflon extrusion developed by General Electric.

Five types of paralleled conductor ribbon cable were arrived at during a conference with C.R. Conner of Methode Electronics, Inc., at their plant in Chicago along with Mr. R. Stabler of DuPont's Film Department, Wilmington, Delaware. These five items are described in Table II. All of the ribbon cable samples are based on polyimide film (DuPont H Film) bonded with perfluoroethylene-propylene resin (DuPont FEP). The FEP is extrusion coated on the H film by DuPont. The ribbon conductors are then sandwiched between two layers with both layers of FEP facing in against the copper. The bond between ML layers is made through thermoplastic adhesion obtained by flowing the FEP around the conductors. A very small sample, essentially like Item 1, was obtained from the contracting officer and found to withstand flexing on a $\frac{1}{4}$ " mandrel in liquid helium without failure. In the hopes of improving the cryogenic flexibility the FEP thickness will be decreased in Item #2. It is not known whether or not a bond can be achieved with a .001 inch FEP coating using .040 inch thick conductors so Item #3 has been proposed in which the conductor thickness has been decreased to .0027 -- the practical minimum. Items #4 and #5 are based on the construction of Item #3 except that they are shielded constructions. The very minimum thickness has been projected for such shield constructions because at best their cryogenic flexibility is expected to be a limiting characteristic.

The parallel conductor ribbon cable samples have just been ordered.

In anticipation of the work on ribbon cable, new and improved mandrels have been made for cryogenic flexibility tests on ribbon up to 1 inch wide, as shown in Figures 1 and 2. Similarly improved mandrels have been made for the cryogenic flexibility tests on round wires as shown in Figure 3. These mandrels provide much better means for clamping the wire. Provision has been made so that round wire will not "pile upon itself" as it sometimes tends to do with the mandrels used previously.

Table II
Ribbon Cable

- Item #1 - will be 400 feet of 1" wide cable consisting of a 2 mil H-Film with 2 mil FEP, as the adhesive, each side, with .004" by .040" conductors on .075" centers.
- Item #2 - will be 50 feet of 1" cable consisting of 1 mil H-Film, with 1 mil FEP as the adhesive, each side, using .004" by .040" conductors on .075" centers.
- Item #3 - will be 150 feet of 1" cable consisting of 1" H-Film and 1 mil FEP, each side, with a .0027" by .040" copper conductor on .075" centers.
- Item #4 - will be 50 feet of the cable described in Item #3 above, and it will be shielded one side using either a 1/2 mil FEP or 1 mil FEP as the adhesive between the screen mesh and the cable. The screen mesh will give the effect of 65% shielding coverage. The dielectric to cover the shield will be either 1/2 or 1 mil FEP as the adhesive with a 1 mil H-Film over the FEP.
- Item #5 - will be 50 feet of the 1" cable as described in Item #3 above and will be shielded on both sides. Construction will consist of 1 mil H-Film with 1/2 or 1 mil FEP as adhesive, a 65% wire mesh screen, a 1/2 or 1 mil FEP, as the adhesive, between the screen and cable, 50 feet of the cable mentioned in Item #3 above, 1/2 or 1 mil FEP as the adhesive, a wire mesh screen which will give 65% coverage, a 1/2 or 1 mil FEP, with 1 mil of H-Film off the top in a sandwich type construction.

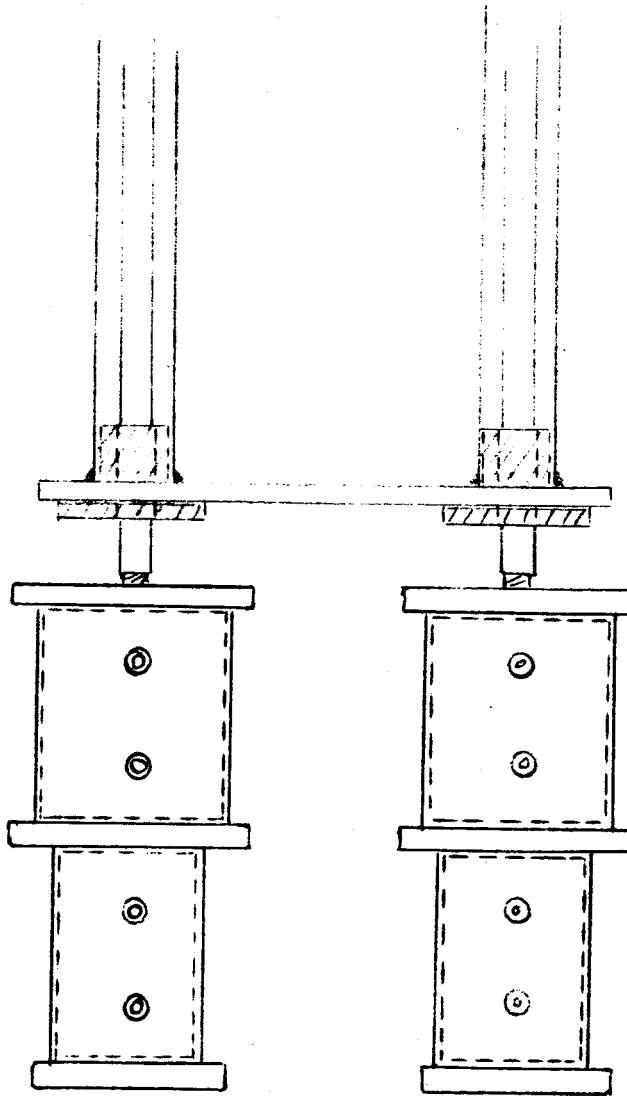
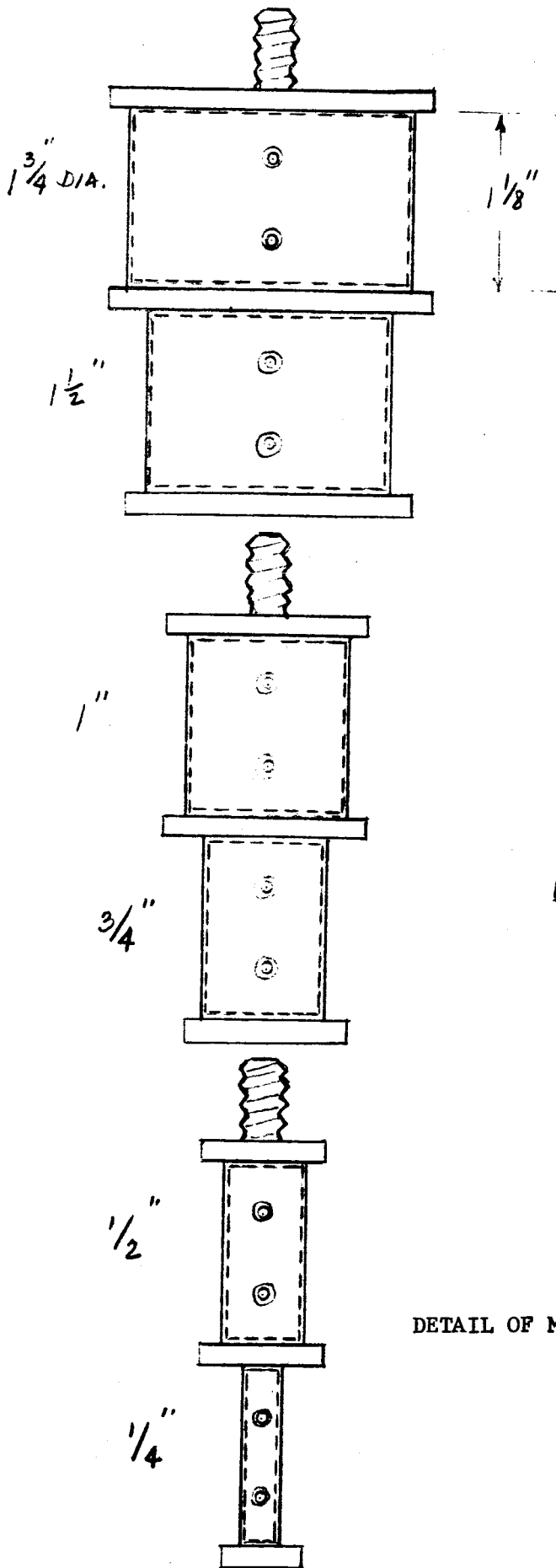


Figure 1.

NEW MANDRELS FOR RIBBON CABLE FLEXIBILITY TEST

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ASSEMBLY :

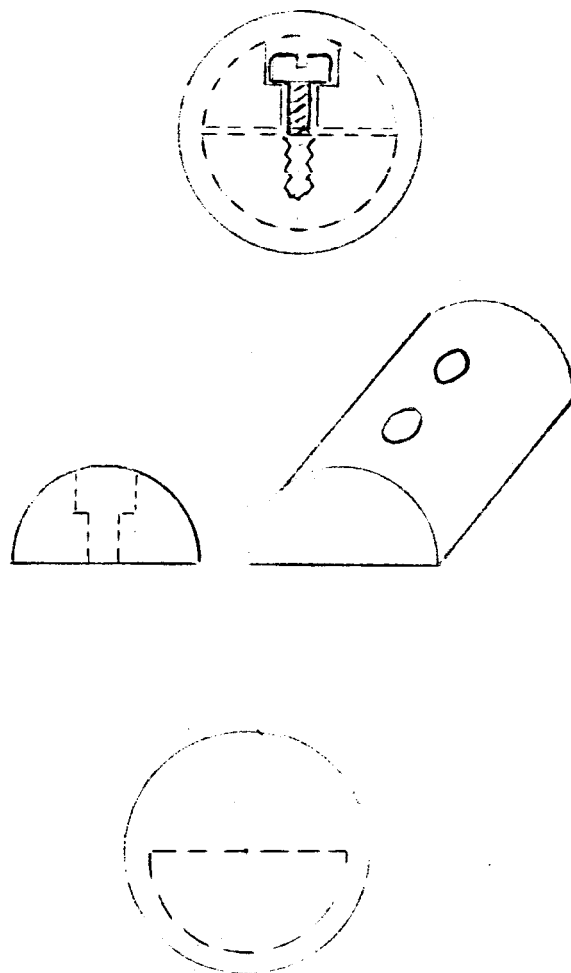


Figure 2.
DETAIL OF MANDRELS FOR RIBBON CABLE FLEXIBILITY TEST

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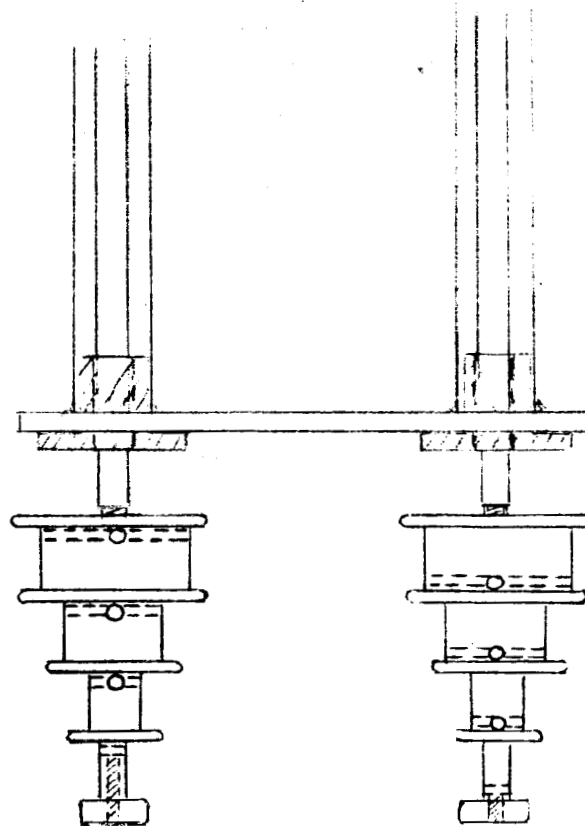


Figure 3.
IMPROVED MANDRELS FOR WIRE FLEXIBILITY TEST

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Purification of Cryogenic Liquids
for
Voltage Breakdown Tests

In the previous work on voltage breakdown of cryogenic liquids, it is recognized that the liquids were probably contaminated with dispersed particles of air. Such tests are useful because the cryogenic liquids in service undoubtedly will often be contaminated. Nevertheless, it is very useful and necessary from the theoretical aspect to determine the effect of such impurities. Blaisse in Delft, Holland, has emphasized the very great importance of such contamination on the dielectric strength of liquid helium and more extensive discussion of the effect of impurities is given in the European report.

During the quarter, equipment has been designed and built (but not yet tested) which makes use of a reflux principle first suggested to the author by Dr. Careri in Rome. The assembled test cell is shown in Figure 4. The equipment is designed so that it may be first evacuated. Pure gas is then admitted and condensed at the bottom by the surrounding cryogenically cooled wall. The liquid at the bottom is then boiled by applying energy to a small heater immersed in it. The rising vapor is then condensed in pure form on a stainless steel condenser, the details of which are shown in Figure 5. The condensed liquid then drips into a Pyrex glass test chamber containing the test sphere gap. The test chamber is equipped with a self-emptying syphon. The details of the syphon and the test cup (without the sphere gap) is shown in Figure 6. When the test cup fills with condensate it will automatically empty and the process will repeat. In this way it is possible repeatedly to wash the test spheres and container with extremely pure liquid. When the heater at the bottom is turned off the process is arrested and dielectric tests can be made on the extremely pure liquid. The liquid can be replaced as often as is desired.

In order to achieve even greater purification than is perhaps possible with just repeated boiling and condensation, a charcoal absorbent has been placed under the test chamber to filter the output liquid. A fritted glass filter prevents possible transfer of charcoal particles to the bulk liquid.

Unlike the ultra-fine pore filtration techniques used by Careri in Rome, with super-fluid helium, the equipment as constructed should be able to purify not only helium but also other cryogenic liquids as well.

Program of October and the Tenth Quarter

In October the first multiple conductor round wire samples are expected and evaluation work will begin. The work on voltage breakdown in ultra-pure cryogenic liquids will be continued also.

These programs will be continued in the quarter and extended to ribbon cable when the samples are received. It is hoped, also, that time will be available for additional measurements of dielectric loss in the cryogenic liquids.

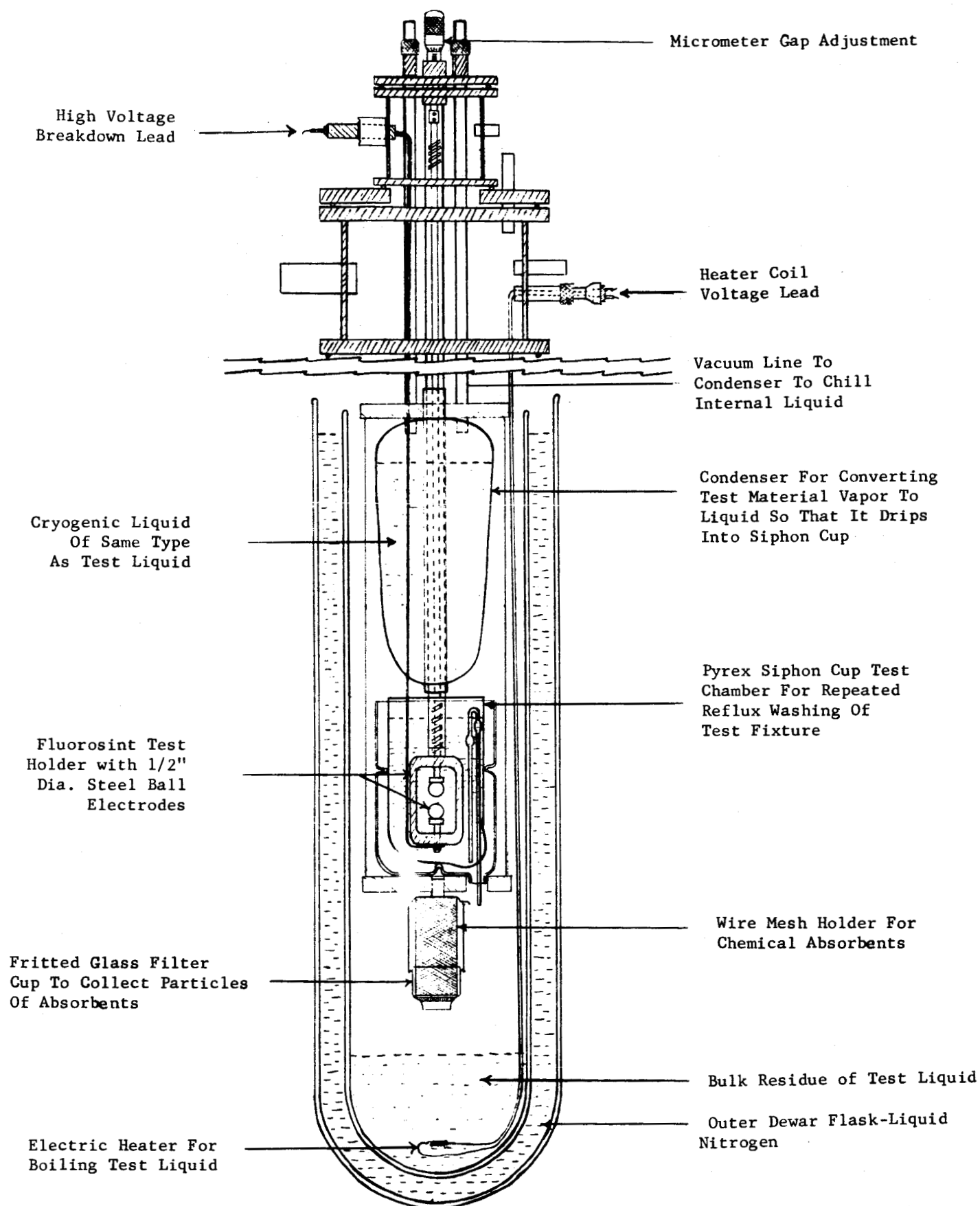
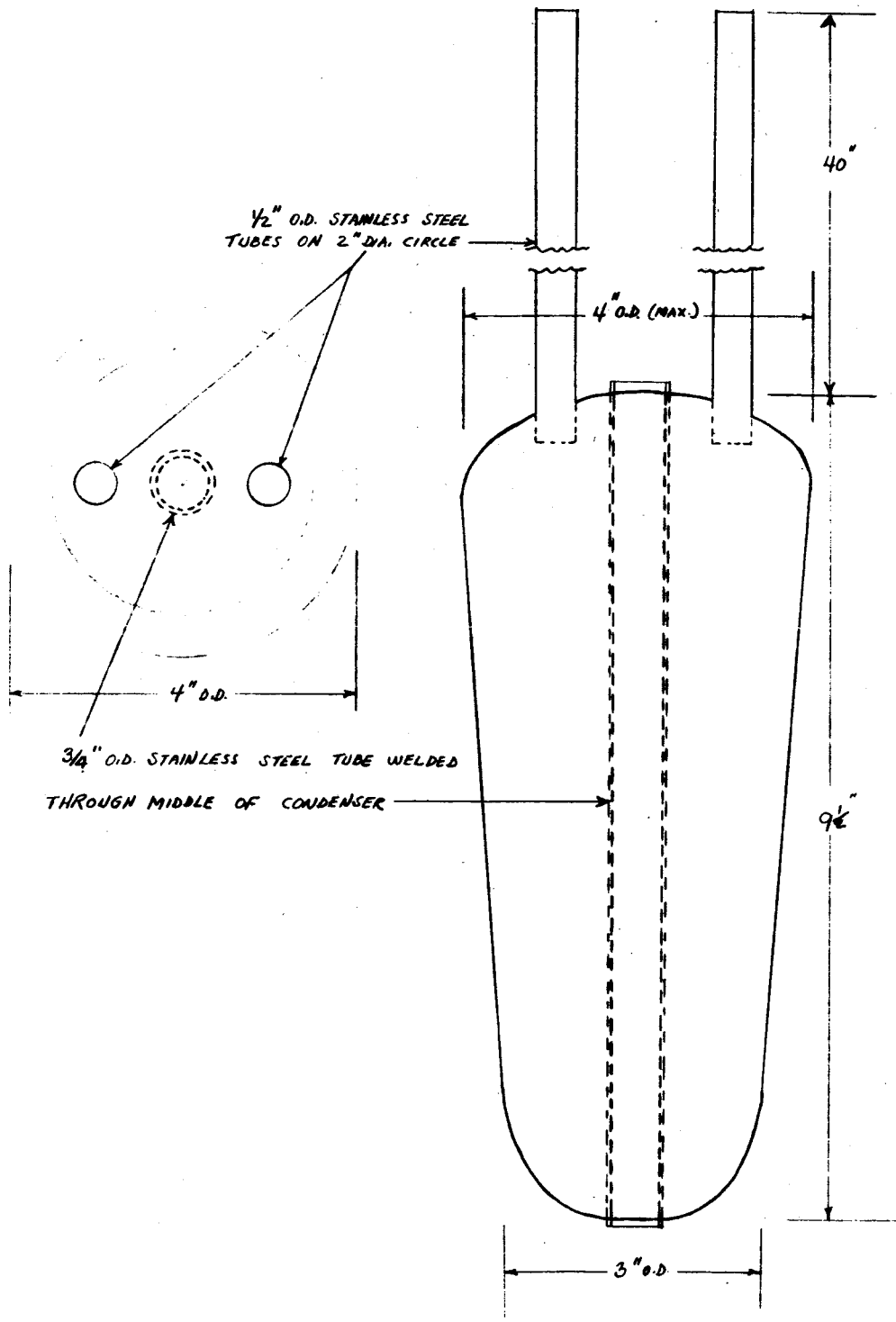


Figure 4.

VOLTAGE BREAKDOWN APPARATUS FOR PURE CRYOGENIC LIQUIDS

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MATERIAL - STAINLESS STEEL

NOTE - THIS CONDENSER MUST BE VACUUM TIGHT.

THE OUTSIDE TUBES MUST BE IN PERFECT ALIGNMENT IN ALL DIRECTIONS WITH THE 3/4" TUBE IN THE MIDDLE OF THE CONDENSER.

Figure 5.
LIQUID CONDENSER - VOLTAGE BREAKDOWN EQUIPMENT
FOR
CRYOGENIC LIQUIDS

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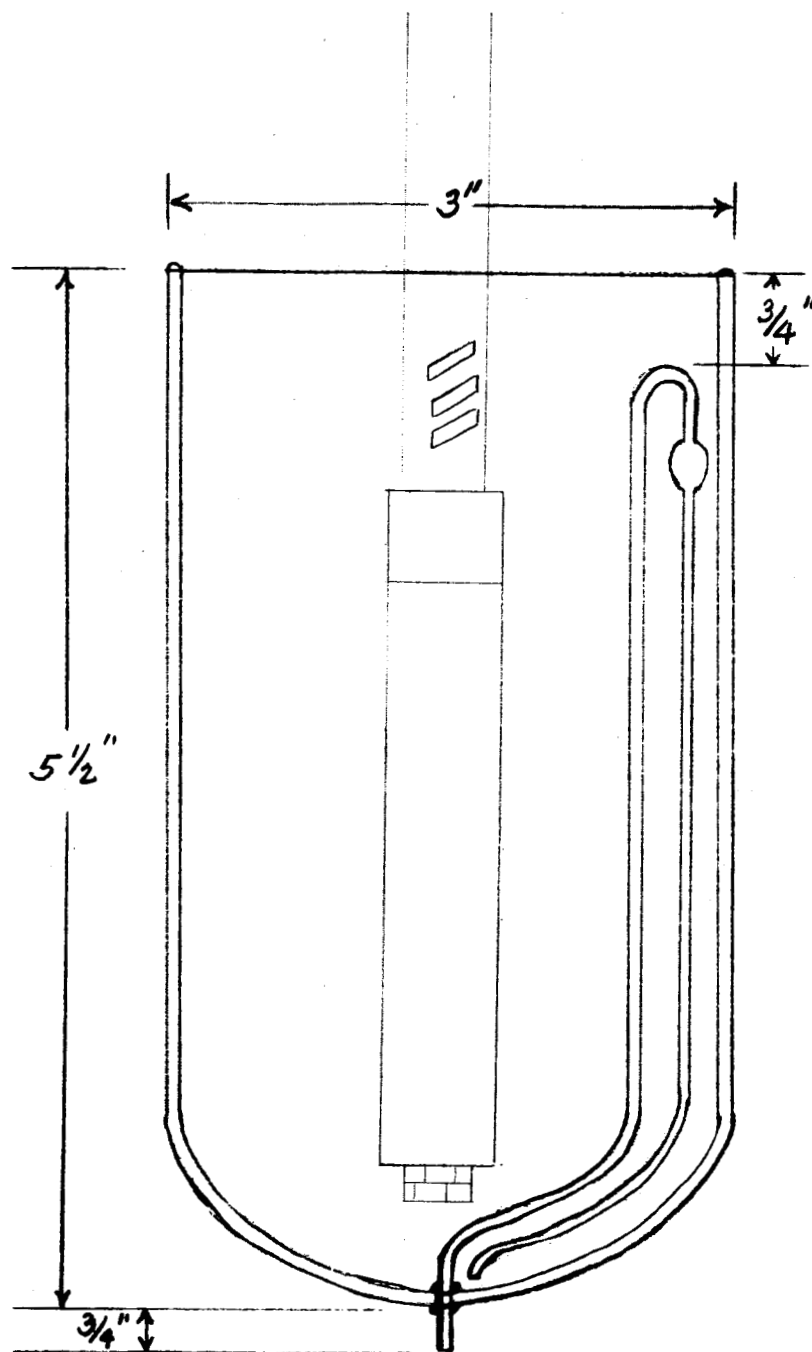


Figure 6.
SIPHON CUP - VOLTAGE BREAKDOWN EQUIPMENT
FOR
CRYOGENIC LIQUIDS

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APPENDIX

DIELECTRICS AT CRYOGENIC TEMPERATURES

A SUMMARY OF EUROPEAN VISITS

INTRODUCTION

In the 8th Quarterly Report, dated July 15, 1963, a chronological summary of the author's recent European visits is given in Appendix A. Appendix A did not contain more than general reference to the technical details discussed. In this report a more detailed discussion of several topics pertinent to the work of the subject contract has been included under the following headings:

1. Electrical Conductivity, Voltage Breakdown and Dielectric Losses in Cryogenic Liquids
2. Electrical Properties of Nonmetallic Materials at Cryogenic Temperatures
3. Physical Properties of Nonmetallic Materials at Cryogenic Temperatures.

These discussions are arranged hopefully in an orderly fashion without reference to the chronology of the visits. The original sources of the information is given including that from the United States even though the reference was suggested by another individual.

Most of the cryogenic information obtained in Europe was quite theoretical in nature. In the author's opinion, such theoretical work is important to the understanding of engineering properties and design. An attempt has been made to interpret the theoretical work in engineering terms.

TECHNICAL DISCUSSIONS

Electrical Conductivity, Voltage Breakdown and Dielectric Loss in Cryogenic Liquids

Conductivity and Ion Mobility

The measurement of electrical conductivity in liquids can be considered broadly to have two principal objections:

1. To provide theoretical understanding of the physical structure of liquids.
2. To provide information concerning the voltage breakdown mechanisms in liquids.

These two objectives are not completely unrelated so both are of interest in the subject work. Most of the studies of conductivity in liquids have

been concerned with the mobility of ions induced by artificial means (i.e., α or γ radiation). However, Chia-Shan Pao⁽¹⁾ has investigated "natural" conductivity in liquid oxygen at 90 K and in liquid iso octane at several temperatures. He found the results to be strongly influenced by field strength as shown in Figures 1 and 2. The measurements were made in the cell shown in Figure 3. Considerable attention was paid to obtaining the purest liquids possible and also an extremely stable voltage source which permitted the measurement of very small currents. Plumley⁽²⁾ had suggested earlier that potential dissociation theory might be used to account for "natural" conductivity. He developed the formula for current:

$$I_A = C_{(exp)} \left[(2e/KT) (e X/300D)^{\frac{1}{2}} \right]$$

where $C \approx$ number of dissociated molecules at 0 field
 X = Field strength in KV/cm
 K = Boltzmann's constant
 e = Unit charge
 D = Dielectric constant of the liquid
 T = Absolute temperature

The curves shown in Figure 4 indicate reasonable adherence to the above formula although Pao has calculated the theoretical slopes of the curves and found some differences with experiment which he attempts to explain. At any rate, the steepness of the curves increase as the temperature decreases. Consequently, at low voltage stress the conductivity of cryogenic liquids is very low. However, as shown in Figure 2, the conductivity of liquid O_2 becomes measurable at voltage stresses of about 6 KV/cm. Similar curves of current versus stress for other cryogenic liquids - particularly liquid hydrogen and helium - would be very interesting. Unfortunately, these data seem not to be available.

Considerable information is available concerning ionization induced conductivity in cryogenic liquids. Much of this work is concerned with helium ions which form an unusual ionic solution in liquid helium. Careri,⁽³⁾ now at the University of Rome, has summarized much of this work. The work of Lothar Meyer⁽⁴⁾ and others is important also. In liquid helium above the λ -point, the mobility of both positive and negative ions is of the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ and about inversely proportional to the viscosity which for helium decreases with decreasing temperature. From these data the diameter of the ion in normal helium is calculated to be about 5 times the gas kinetic diameter of the helium molecule.

(1) "Conduction of Electricity in Highly Insulating Liquids", Chia-Shan Pao, Phys. Rev., Vol. 64, Nos. 3 & 4 (Aug. 1 & 15, 1943), pp 60-74.

(2) H.J. Plumley, Phys. Rev. 59, 200, (1941).

(3) "Progress in Low Temperature Physics - Chap. II Helium Ions in Liquid Helium II", (book) Amsterdam: North Holland 1961, pp 58-79.

(4) "Mobilities of He Ions in Liquid Helium", Meyer & Reif, Phys. Rev., Vol. 110, No. 1, pp 279-280 (April 1, 1958).

"Ion Motion in Superfluid Liquid Helium under Pressure", Meyer & Reif, Phys. Rev., Vol. 123, No. 3, pp 727-371 (Aug. 1, 1961).

"Ions in Liquid Helium", L. Meyer, Proc. VII Int. Conf. Low Temp. Physics, Toronto, 1960, pp 487-495.

"Kinetic Theory of Dense Fluids, XII, Electronic and Ionic Motion in Liquid He I and Liquid He³", Davis, Rice & Meyer, V. of Chem. Phys. Vol. 37, No. 7, pp 1521-1527, (Oct. 1, 1962)

(4) continued on next page.

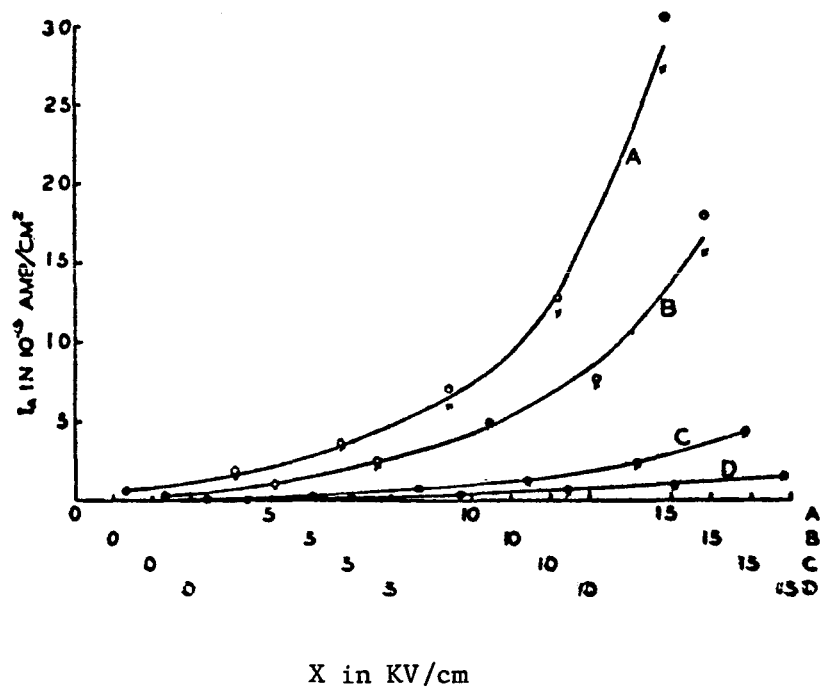


Figure 1. Variation of residual current with field strength at constant temperature. Curves A, B, C, and D represent the results when $T = 309.5$, 296.7 , 273 , and 195 K, respectively. Open circle and cross represent the results for positive and negative voltages applied to the high voltage electrode.

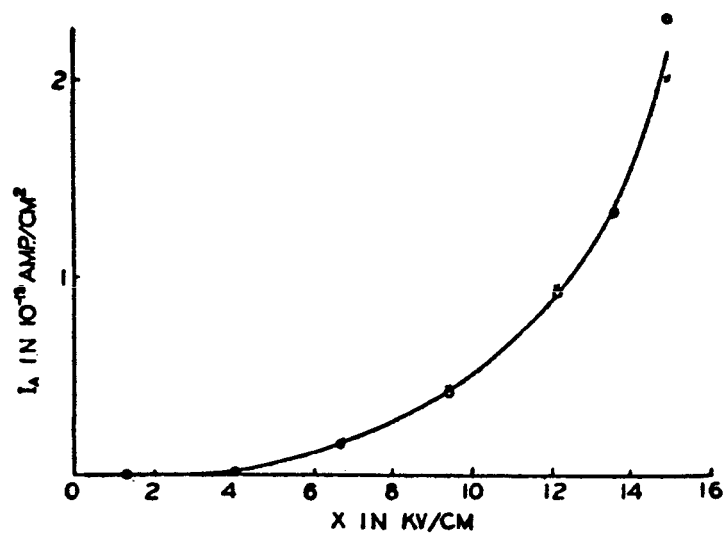


Figure 2. Variation of the residual current with field strength in liquid oxygen. Open circle and cross represent the respective results for positive and negative voltages applied to the high voltage electrode.

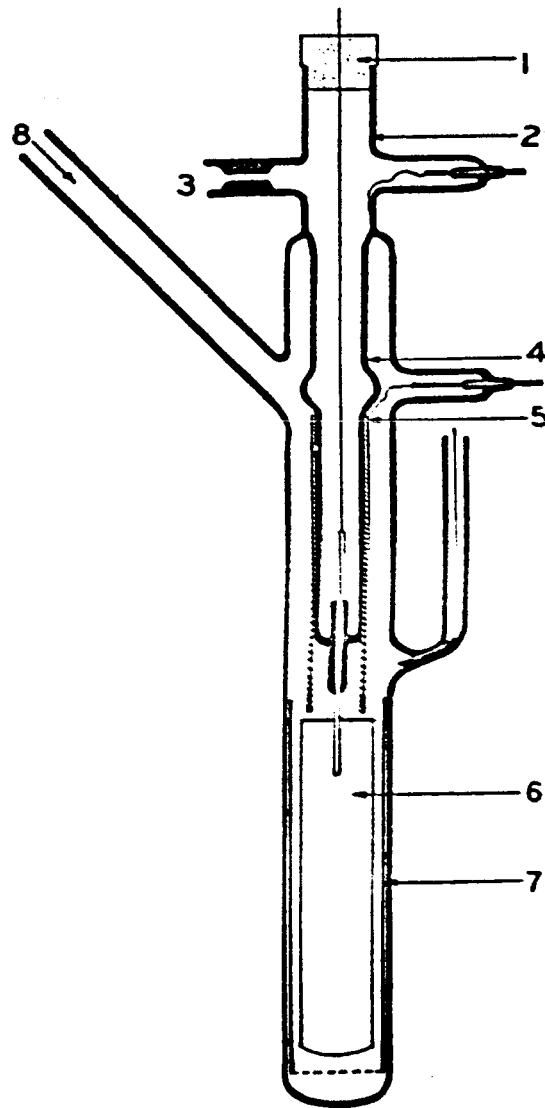


Figure 3. Experimental cell IV: (1) amber plug, (2) Aquadag film, (3) to diffusion pump, (4) Hanovia "Liquid Bright Platinum" paint serving as a guard ring, (5) brass cylinder, (6) dural rod, (7) monel cylinder, (8) glass tube connected to a two-way stopcock.

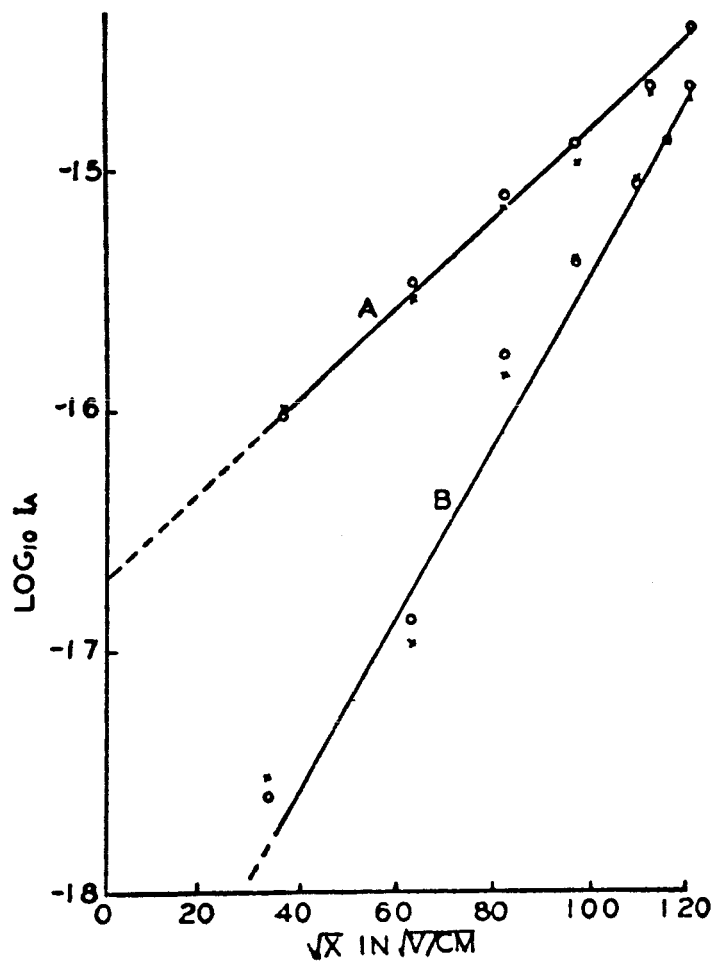


Figure 4. Relation between $\log_{10} I_a$ and $X^{\frac{1}{2}}$. Curve A represents the results for isooctane at $T = 273^{\circ}\text{K}$ and curve B represents the results for liquid oxygen at $T = 90^{\circ}\text{K}$. Open circle and cross represent the respective results for positive and negative voltages applied to the high voltage electrode.

In helium below the λ -point (2.19°K) the character of ions becomes very complex and the study may be divided into two principal parts.

1. The motion of ions as a means for studying the physical nature of super-fluidity.
2. The nature of the ions themselves.

As the temperature is decreased below the λ -point, the ion mobility at low field stresses (less than 1 KV cm^{-1}) increases very rapidly as shown in Figure 5. Positive ions possess a slightly higher mobility than negative ions. Although different ideas have been advanced, it is generally concluded that the positive ion is a cluster of helium ions polarized around the charge, and that the negative ion is an electron trapped within a shell of polarized atoms. On the basis of magnetostriction measurements it has been calculated that a single charge is bound to about 50 helium atoms in superfluid helium.

More detailed consideration has been given to the complex structure of the ions and the changes with temperature. Unlike the situation at low field strength, ionic mobility in liquid helium is influenced by high field strengths. Williams and Stacey⁽⁵⁾ have found that x-particle induced conductivity in liquid helium is independent of temperature between 1.4 and 4.2 K when measured at stresses above 10 KV cm^{-1} . Apparently the ions reach a critical maximum velocity. Careri⁽⁶⁾ has measured mobility of the positive ion at 0.2 K by magnetic beam deflection. His results are summarized in Figure 6. A small field dependence even at low field stresses is indicated at the very low temperature. However, the relatively low values of mobility as compared to values which would be extrapolated from Figure 5 are even more surprising. Careri⁽⁷⁾ and others have conducted refined experiments on some surprising effects of field strength on the mobility of positive ions in liquid helium. Typical results are plotted in Figure 7 in the conventional fashion. In Figure 8 the results are plotted as a function of drift velocities and extended so as to show the presence of two discontinuities -- the second one at almost exactly twice the velocity of the first. Careri does not have very firm explanations for this most interesting phenomenon, but along with other ideas, he does suggest a relationship to flow phenomena in superfluid helium. However, he has recently determined⁽⁸⁾ that rotating helium is strongly anisotropic to the passage of the negative ion but not to the positive ion.

(4) Continued from previous footnote No. (4) on Page 14.

"Mobility of Ions in Liquid He^4 , I and He^3 as a Function of Pressure and Temperature", Meyer, Davis, Rice and Donelly, Phys. Rev., Vol. 126, No. 6, pp 1927-1939 (June 15, 1962).

(5) R.L. Williams and F.D. Stacey, Canad. J. of Phys. 35, pp 134 & 928.

(6) "Magnetic Deflection of Positive Ions in Liquid Helium at 0.2 K", Careri, Dupre' and Modena, Il Nuova Cimento, Series X, Vol. 22, pp 318-325 (October 16, 1961).

(7) "Critical Drift Velocity of Ions in Liquid Helium", Careri, Cunsolo & Mazzoldi, Phys. Rev. Letters, Vol. 7, No. 5, pp 151-153 (Sept. 1, 1961).

(8) "Ions in Rotating Liquid Helium II", Careri, McCormick & Scaramuzzi, Physics Letters, Vol. 1, No. 2, pp 61-63 (April 15, 1962).

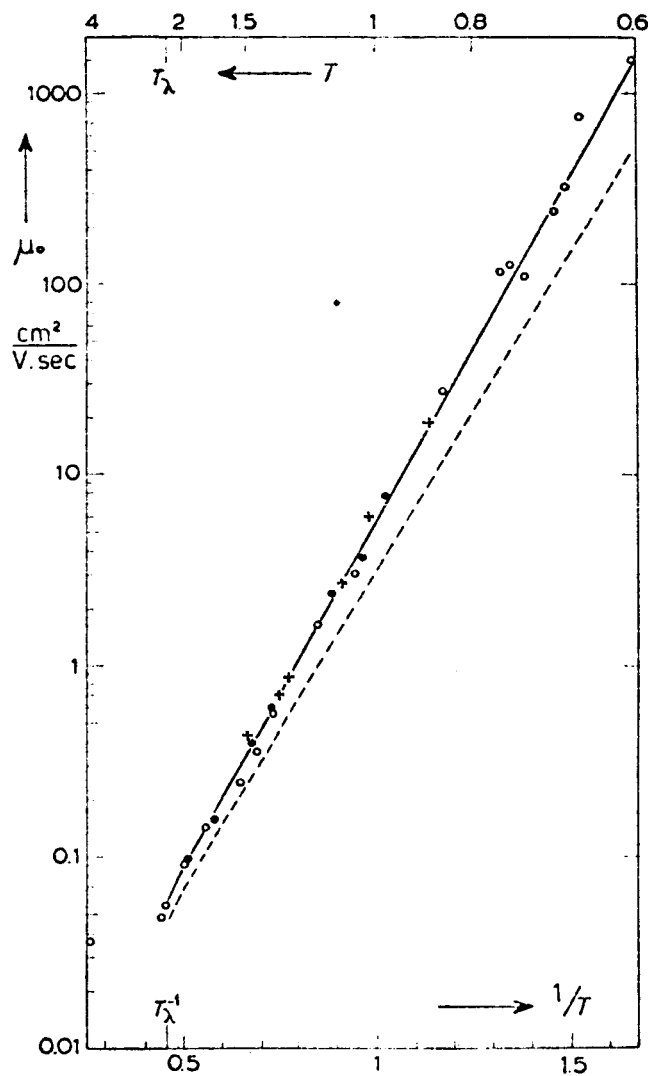


Figure 5. Experimental values of the mobility of positive ions versus the inverse of absolute temperature. White circles from Meyer and Reif data; crosses from Padua (Careri) by space charge; black circles from Padua by heat flush. The dotted line gives the similar data from the negative ions. The experimental points are not shown for sake of clarity.

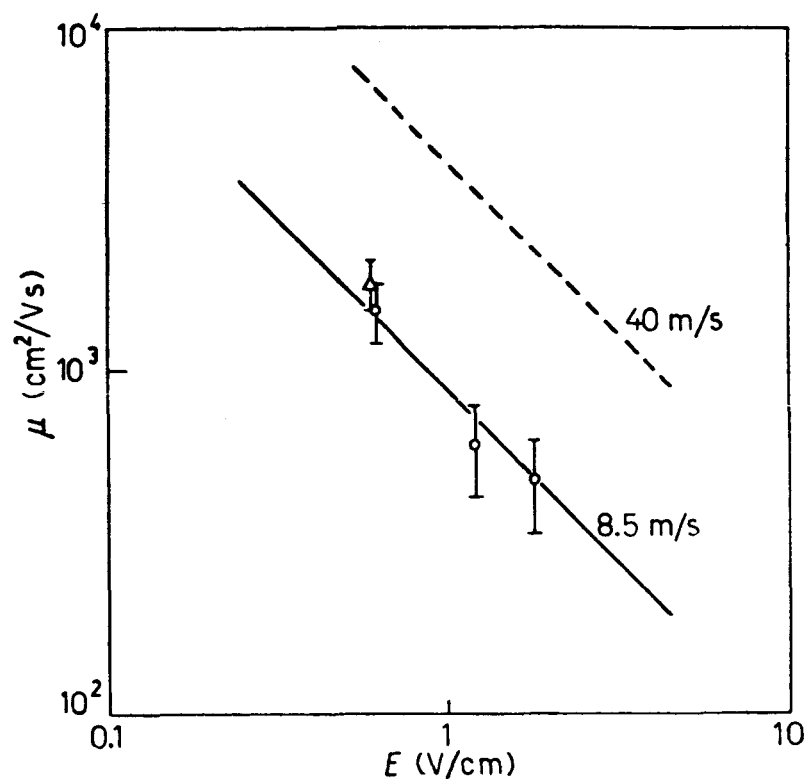


Figure 6. Positive ion mobility in helium at 0.2 K. All points have been measured with a B of 17 kG. The point marked with a triangle has been obtained with a reversed magnetic field. The dotted line is the limiting velocity as quoted by Reif and Meyer.

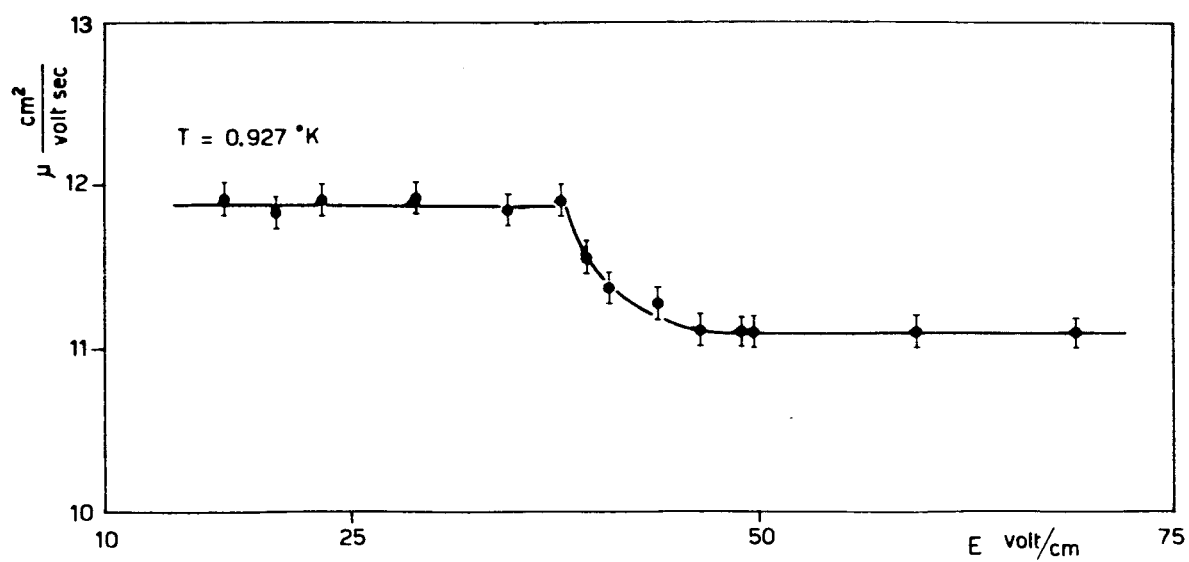


Figure 7. Experimental values of the mobility at $T=0.927^\circ\text{K}$ as a function of the applied electric field E .

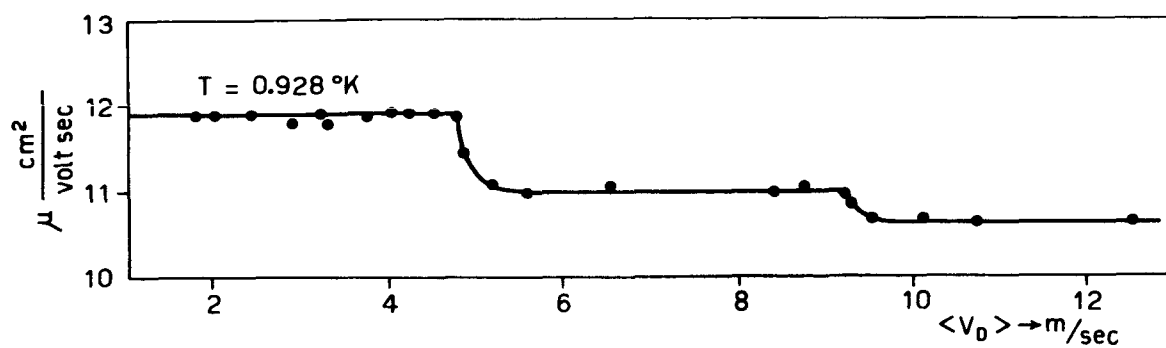


Figure 8. Plot of mobility versus drift velocity at different temperatures.

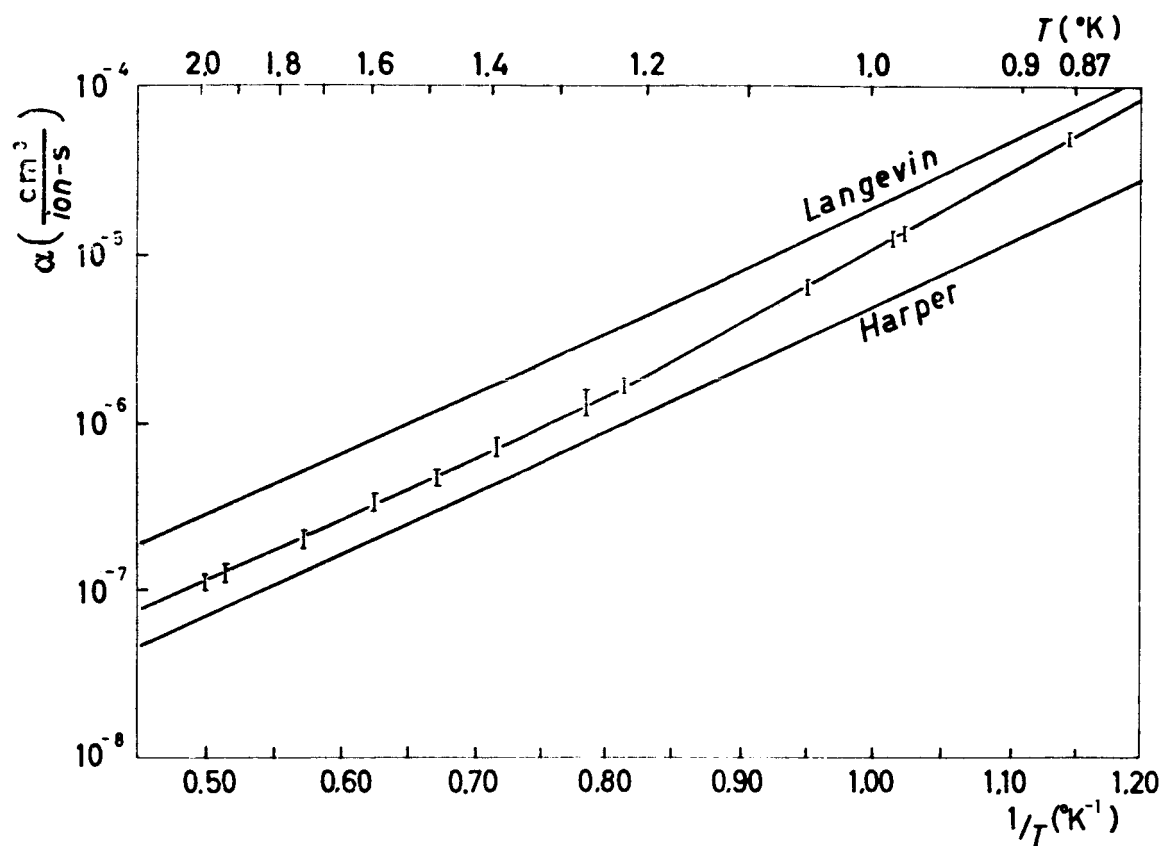


Figure 9. Volume recombination coefficient of ions in liquid He vs. the inverse of absolute temperature. The upper and the lower lines give the values calculated from Langevin's and Harper's theory respectively. The central curve is the best fit of the experimental results.

Swan⁽¹²⁾ has collected data on ionic mobility in liquids from several sources. The data for n-hexane at 19 C (from Growski and Terlecki 1959) is interesting for comparison.

Ion Mobility ($\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$) for n-hexane

<u>Positive Ion</u>	<u>Negative Ion</u>
4.1×10^{-4}	1.3×10^{-3}

T.J. Lewis of Queen Mary College, London, indicated during conversation that mobilities in liquid nitrogen were of the same order as that in hydrocarbons. Unfortunately, no information on ion mobility in liquid neon or hydrogen seems to exist. From the foregoing, it is apparent that ionic mobility is very high in Argon, Krypton and Xenon and is comparable to that of Helium II well below the λ point. Limiting critical velocities of the order of 10^6 cm/sec at stresses above 5 KV/cm have been found for ions in liquid argon. However, unlike mobility in helium, the ionic mobility in A_2 , K_2 & Xe increases with increased temperature as it does also in hydrocarbon liquids. As in helium, ionic mobility may be related to viscosity but this explanation alone is not theoretically adequate. The nature and the size of ions, particularly in dielectric liquids other than helium, seem to be open to considerable question. While the "trap" theory described for helium is possible with these liquids, also, it may also be postulated that the electron moves by jumps between molecules (or atoms). Perhaps both phenomena occur.

In all of the foregoing it is assumed that only very pure liquids are considered. J.A. Kok during discussions in Eindhoven, Holland, described his theory that impurity particles in liquids collect charges and migrate under the influence of electric stress to set up "bridges" which influence breakdown voltage. Blaisse at Delft, Holland, stressed the importance of impurities in reference to the breakdown voltage of liquid helium. Careri discussed the point, also, during the visit to Rome but he felt that such impurities would rather quickly "plate out" (collect at the electrode) under the influence of a low DC stress and that the decreasing transport current should be measurable at least for a short while after the application of voltage.

Voltage Breakdown

Unlike the situation with gases, the voltage breakdown of liquids is still not very well understood. Swan has summarized the "state of the art" and grouped the breakdown mechanisms of liquids under three general headings.

1. Production of free electrons in the gap by electron emission from the cathode.

 (11) "On the Kinetic Theory of Simple Dense Fluids. XI. Experimental and Theoretical Studies of Positive Ion Mobility in Liquid A_2 , K_2 & Xe ", Davis, Rice & Meyer, J. Of Chem. Phys., Vol. 37, No. 5, pp 947-956 (Sept. 1, 1962).

"On the Kinetic Theory of Dense Fluids. XIII. The Mobility of Negative Ions in Liquid A_2 , K_2 & Xe ", Davis, Rice & Meyer, J. of Chem. Phys., Vol. 37, No. 10, pp 2470-2472 (Nov. 15, 1962).

(12) "A Review of Recent Investigations into Electrical Conduction and Breakdown of Dielectric Liquids", D.W. Swan, Brit. J. of App. Phys., Vol. 13, (1962), pp 208-218.

2. The acceleration of the free electrons by the field and the loss of energy through collisions with liquid or impurity molecules.
3. Ionization leading to instability (opinion differs as to whether such ionization occurs in the liquid or in a gas bubble produced in the liquid).

He very wisely points out that each of these processes may be considered as a necessary but not sufficient condition for breakdown, and that the dominant process may be changed by altering the experimental conditions.

Lewis and his co-workers at Queen Mary College, London, are carrying out a very comprehensive program on the mechanism of voltage breakdown in liquids. The emphasis on experimental investigation of many variables as a means to development of the theory is refreshing. The breakdown of the cryogenic liquids - argon, oxygen and nitrogen (and mixtures thereof) has been studied extensively for several reasons. Such gases are simple structures and cannot carbonize or build up deposits on electrodes as hydrocarbons can. Moreover, as mentioned earlier in this report, ion mobility in argon is high as compared to the other gases so that the influence of ion mobility on breakdown voltage can be studied.

Swan and Lewis have intensively studied the effect of electrode material and condition on breakdown voltage⁽¹³⁾. In all cases, a slowly increasing DC voltage was used. Spherical electrodes 0.5 cm in diameter were buffed with increasingly fine grades of chrome-oxide, polishing compound until in the last step no compound was used.* The electrodes were then washed in dust-free hexane and kept under hexane to prevent oxidation. For some measurements, the electrodes were allowed to oxidize for predetermined times in dry air in a dessicator before immersion in hexane. The test chamber and sphere were evacuated to at least 10^{-3} Torr for 18 hrs., then flushed with gas, and evacuated again before the gas was condensed to liquid for test.

The very marked effect of platinum versus stainless steel electrodes on the breakdown of cryogenic liquids (at their boiling points) is shown in Figures 10 and 11. The reversal of the electric strengths for liquid nitrogen and oxygen is particularly noteworthy. Where additional non-oxidized electrode materials are used, the situation becomes even more complex as illustrated in the following table.

- - - - -

- (13) "Influence of Electrode Surface Conditions on the Electrical Strength of Liquified Gases", Swan & Lewis, J. of Electrochem. Soc., Vol. 107, No. 3, pp 180-185 (March, 1960).

* NOTE: It should be pointed out here that J.A. Kok, during conversations at Eindhoven remarked that he believed polishing compound residues affected the values of electric strength obtained by Lewis.

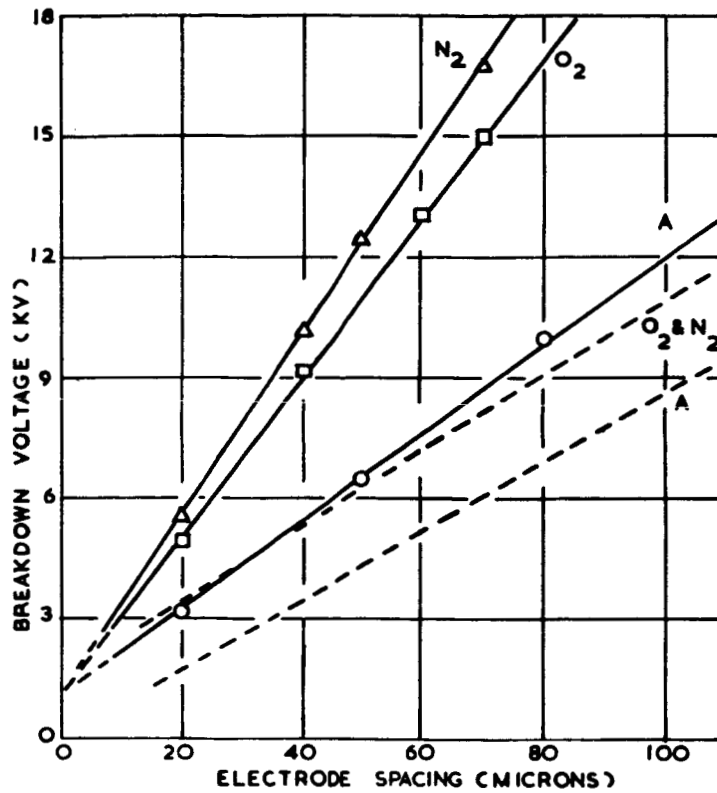


Figure 10. Breakdown voltage vs. electrode spacing with platinum electrodes. O, Argon; □, oxygen, Δ, nitrogen. - - - Results from Kronig & Van deVooren.

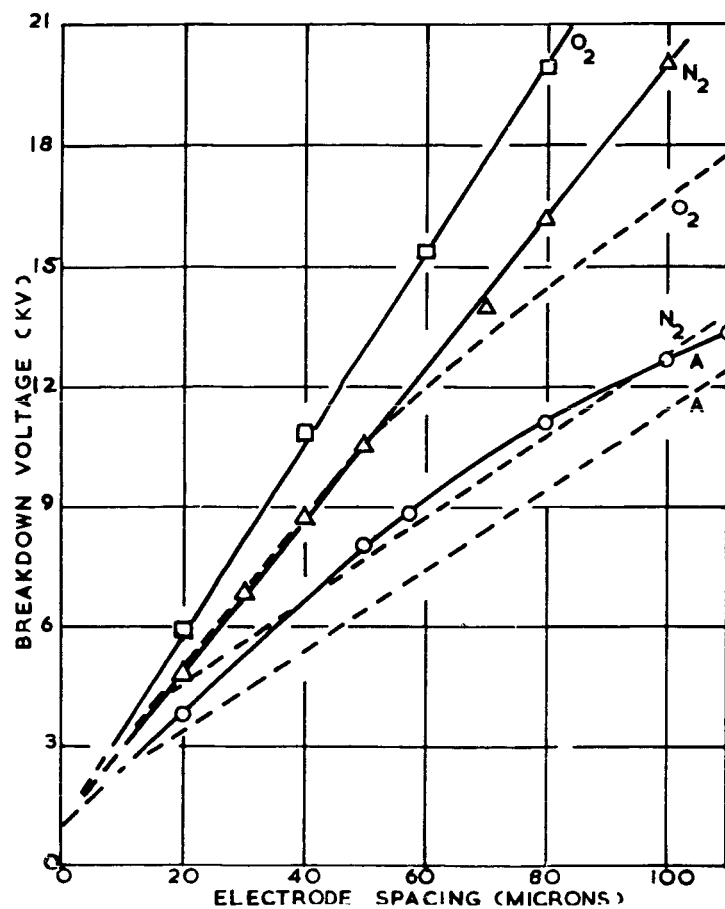


Figure 11. Breakdown voltage vs. electrode spacing with stainless steel electrodes. \circ , Argon; \square , oxygen; \triangle , nitrogen. - - - Results from Kronig and Van deVooren.

MEAN ELECTRIC STRENGTH AS A FUNCTION OF ELECTRODE MATERIAL

<u>Electrodes</u>	<u>Work Function, ev</u>	<u>Electric Strength, mv/cm</u>		
		<u>Argon</u>	<u>Oxygen</u>	<u>Nitrogen</u>
Stainless Steel	-	1.40	2.38	1.88
Brass	-	1.01	1.44	1.62
Copper	4.47	1.40	1.81	-
Gold	4.58	1.16	1.24	1.50
Platinum	5.29	1.10	2.00	2.24

In this table a reversal in order of rating occurs for the different gases even with gold and platinum electrodes which would be expected to have stable, oxide-free surfaces. No correlation exists with work function. In fact, with Argon exactly the reverse of the expected relationship is found.

In order to study such electrode effects further and to separate cathode and anode effects, Swan and Lewis have concentrated on the study of liquid Argon.⁽¹⁴⁾ The effect of oxidation on various metal electrodes in determining electric strength of liquid argon is shown in Figure 12. As expected, oxidation at room temperature does not affect gold or platinum electrodes. The results for the other metals are startling -- particularly the maxima in the curves as a function of oxidation time. Although the effect of an insulating layer on the cathode is most plausible, an anode effect was suspected also and proved to exist as shown in the following table.

Table I
ELECTRIC STRENGTH OF LIQUID ARGON
WITH
ANODE AND CATHODE OF DIFFERENT MATERIALS

<u>Cathode Material</u>	<u>Anode Material</u>	<u>Electric Strength (mv/cm)</u>
Aluminum (15)	Aluminum (15)	0.69
Aluminum (15)	Stainless Steel (15)	1.44
Stainless Steel (15)	Aluminum (15)	0.88
Stainless Steel (15)	Stainless Steel (15)	1.86
Stainless Steel (0)	Gold	1.22
Stainless Steel (17)	Gold	1.26

(The time of electrode oxidation is indicated in brackets - minutes)

The ratio of the maximum to minimum value of electric strength, 2.7, for the various combinations shows how important electrode characteristics can be, particularly where it is recognized that with hydrocarbon liquids such effects are very much less marked and in the case of anode, effect practically negligible.

(14) "The Influence of Cathode and Anode Surfaces on the Electric Strength of Liquid Argon", Swan & Lewis, Proc. of Phys. Soc., Vol. LXXVIII pp 448-459.

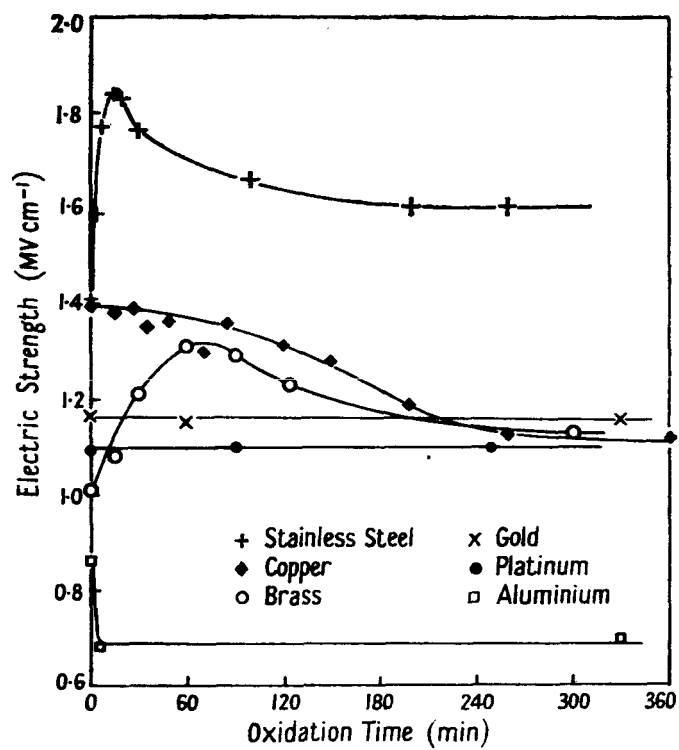


Figure 12. Electric strength of liquid argon with oxidized electrodes.

The effect of oxidation time on the cathode and anode effects is shown in Figure 13 and replotted in Figure 14 as a function of log time. It is apparent that the "intrinsic" electric strength of liquid argon is not a meaningful quantity since so many factors affect voltage breakdown.

Dissolved oxygen in argon (and also in nitrogen) has a considerable effect on the breakdown voltage of liquid argon as shown in unpublished information obtained from Lewis in London (Figure 15). Lewis postulates that when oxygen is present in argon a strong electron attachment process exists which, in consequence, increases the electric strength. It is apparent from the following table that quite small quantities of oxygen have a considerable effect as would be expected.

Table II
ELECTRIC STRENGTH OF LIQUID ARGON-OXYGEN MIXTURES
WITH
ALUMINUM AND STAINLESS STEEL ANODES AND A PLATINUM CATHODE

<u>Argon</u>	<u>% Oxygen</u>	<u>Electric Strength (mv/cm)</u>		<u>Difference in Strength (mv/cm)</u>
		<u>Aluminum Anode</u>	<u>Stainless Steel Anode</u>	
Commercial	20	1.35	1.71	0.36
Commercial	1	1.33	1.68	0.35
Commercial	.002	0.686	1.07	0.384
Spectroscopic	.0002	0.764	0.888	0.124

In summary, it seems reasonable to assume that the character of the cathode will influence the electric strength of cryogenic liquids through the process of electron emission into the liquid. The anode exerts an influence only if the rate of electron emission from the cathode is greater than the anode can accept. In this case, a high space charge will develop in the vicinity of the anode so that the breakdown voltage is decreased. Probably the anode space charge forms only when part of the breakdown current is carried by negative oxygen ions. A more detailed analysis has been developed by Swan⁽¹⁴⁾ and his hypotheses are quoted as follows:

"The experimental curves in Figure 12 can now be explained as follows. For zero oxidation time with stainless steel and brass electrodes the anode is not important in the breakdown process since the surface layer is not sufficiently insulating to prevent ion neutralization. This results in practically no anode space charge and the actual breakdown strength is determined by the emission properties of the cathode and by the positive ion space charge set up there by ions produced uniformly in the bulk of the liquid. As the oxide layer on the electrodes increases in thickness the cathode emission is reduced, and if the anode space charge is still insignificant a rise in the electric strength will result. When the electrode layers are sufficiently thick the emission from the cathode could exceed that accepted by the anode, resulting in an anode space charge field enhancement and an increased x value. The strength now depends more upon the anode surface condition than upon the cathode.

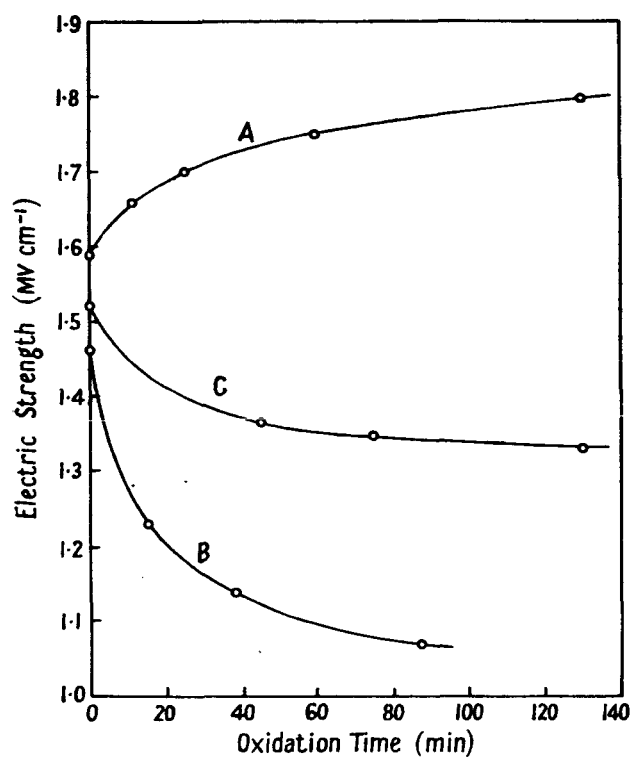


Figure 13. Influence of anode and cathode on the electric strength of liquid argon. A, Cathode stainless steel, various oxidation times; anode stainless steel, zero oxidation time. B, Cathode gold; anode stainless steel, various oxidation times. C, Cathode stainless steel, 24 hour oxidation time; anode stainless steel, various oxidation times.

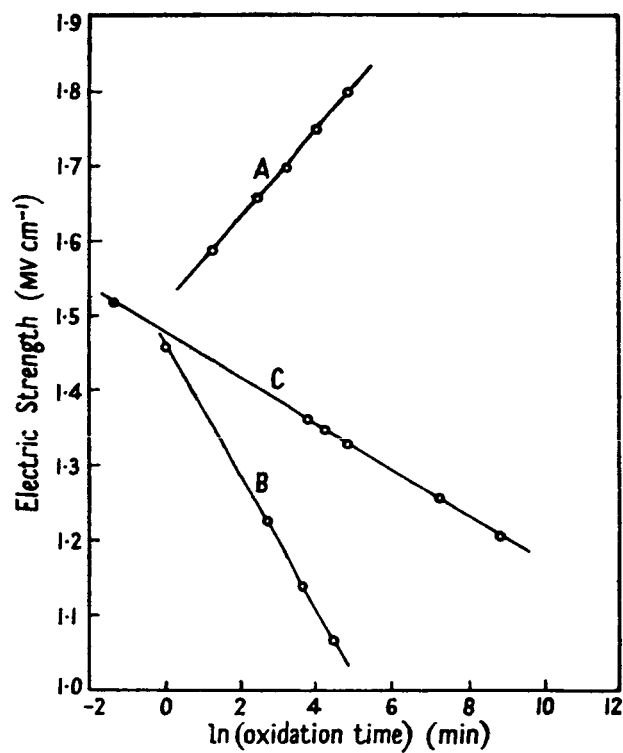


Figure 14. Influence of cathode and anode oxidation on the electric strength of liquid argon. The electrode conditions are as given for Figure 13.

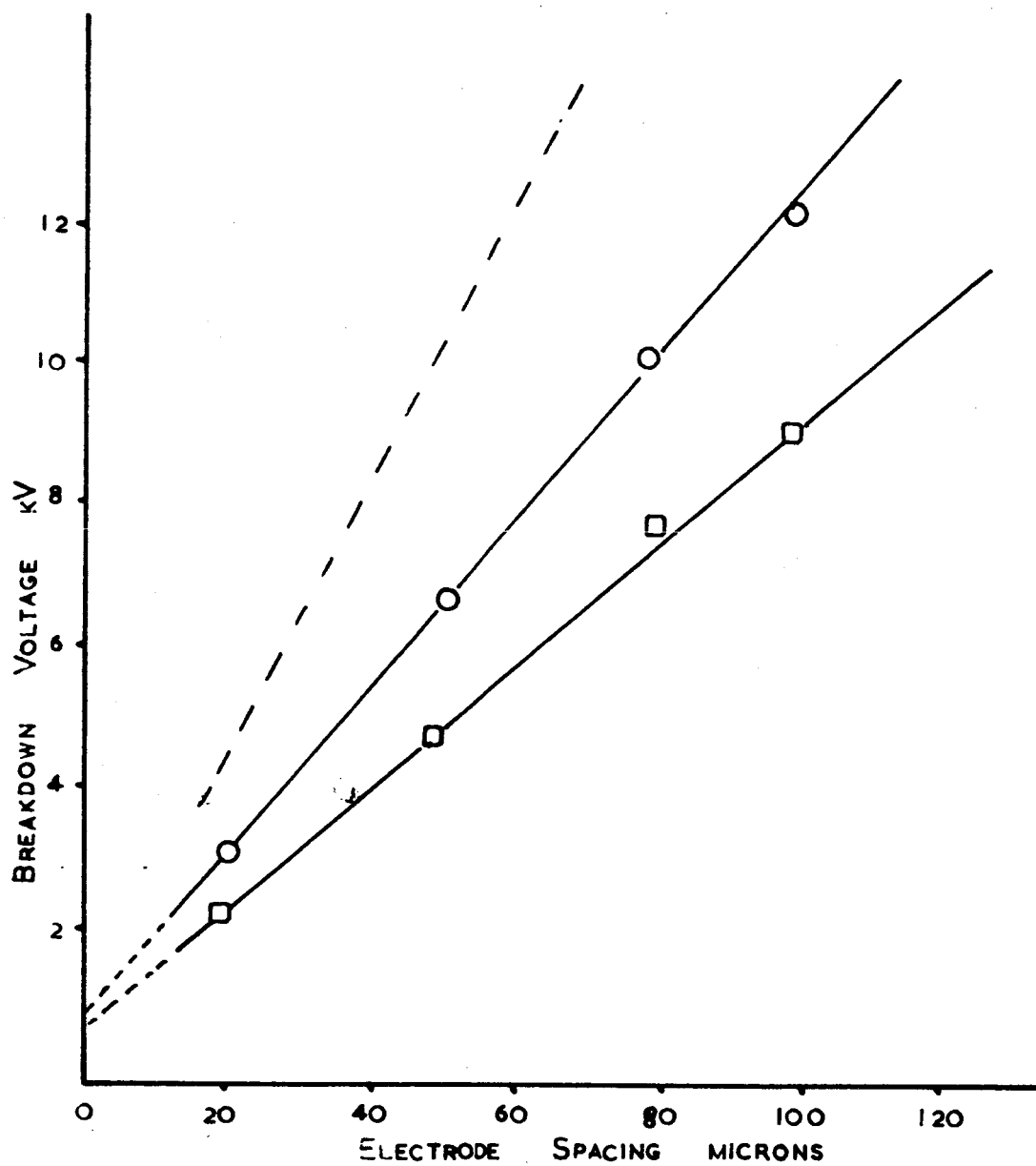


Figure 15. Variation of breakdown voltage with electrode spacing.

□ Oxygen-free argon ○ Normal argon.

- - - 5 μ sec square pulses

Further increase of oxide layer increases simultaneously the space charge field at the anode and the production of positive ions in that region. The mean electric field required for breakdown is therefore reduced. Curves A and B of Figure 13 can be explained in similar terms. The absence of the initial cathode-dependent range when using copper and aluminium electrodes (Figure 12) can be explained if it is assumed that even at zero oxidation time the anode surface is sufficiently insulating to set up an appreciable space charge. With platinum and gold electrodes it is not possible to deduce whether the anode or the cathode is predominant since no variation with oxidation time was observed. However, the last two results in Table 1 suggest that a gold anode can give rise to a space charge since if the cathode had been the controlling electrode in these experiments the measured electric strength should have been much greater in magnitude. The existence of an insulating surface layer on gold has been proposed by Green (1955), who found that his results for the conduction current in n-hexane with gold electrodes could be explained in terms of an adsorbed hydrocarbon layer. It is quite possible that during electrode preparation a chemisorbed hydrocarbon layer could have been formed, thus giving rise to the observed effects.

If it is assumed that the law relating I_a to anode field is some rapidly increasing function of field, then, once a space charge has been established for a given pair of electrodes and fixed applied field, the magnitudes of the space charge field will not be very dependent on oxygen concentration. An increase in the rate of arrival of negative ions will be compensated for by a small change in anode field. Consequently, in this case, the influence of the anode on the measured breakdown will be almost independent of oxygen concentration. The results in Table 2 confirm this. For commercial argon and argon with greater concentrations of oxygen, the strength increases with increasing oxygen content but the difference in strength due to different anode materials remains the same. The increase in strength with increasing oxygen content can, in this range, be attributed to a reduction in the number of electrons as a result of attachment in the liquid as discussed earlier. When the oxygen concentration is very small and ion formation in the liquid is less probable, no appreciable space charge is formed and the influence of the anode is reduced. From Table 2 it can be seen that for the spectroscopically pure argon the change in strength due to the different anodes was reduced to 30% of that observed at large oxygen concentrations. That a difference was still found suggests that, even in the purer argon, electron attachment was occurring, although at a very much reduced rate. For a stainless steel anode the strength increases continuously with increasing oxygen content, but with an aluminium anode there is a reduction in strength for very small oxygen concentrations which is followed by a continuous increase with the addition of more oxygen. This behavior suggests that a stainless steel surface of zero oxidation time does not give rise to an anode space charge, so that the continuously increasing strength observed with increasing oxygen content and a stainless steel anode can be attributed to progressively increased electron attachment in the liquid. Aluminium, however, forms a highly insulating surface layer immediately on the exposure to air. It is to be expected, therefore, that a space

charge would form even at very low oxygen concentrations when only a small percentage of the electrons emitted form ions, and as a result of this an appreciable anode field enhancement could be set up during the period of voltage increase prior to breakdown. In this situation the x process would increase and the strength decrease with increasing oxygen concentration until attachment in the body of the liquid became predominant. At this point the effective reduction in x outweighs the increase due to the anode space charge, and the strength increases in a similar way to that observed with a stainless steel anode.

The effect of space charges can, of course, be studied with impulse voltages. Lewis has recently extended his work to include impulse studies and provided some additional information which was sketched during the meeting in London. Some of these data have been added as a dashed line to Figure 15. Additional data from Lewis are reported as sketched (from notes) in Figures 16 and 17. (NB.- These values should not be taken too literally.) As shown by the cross overs in Figure 16 and the maxima in Figure 17, space charge effects are related to the oxide thickness on the electrodes.

Very recently Lewis has repeated the study of electrode effects using liquid methane (CH_4 , BPt-161.5C, 111.5K), -- the very simplest of the hydrocarbon liquids. His unpublished data obtained during the conference in London follows:

TABLE III
ELECTRIC STRENGTH OF LIQUID METHANE
WITH
ANODE AND CATHODE OF DIFFERENT MATERIALS

<u>Cathode Material</u>	<u>Anode Material</u>	<u>Electric Strength - mv/cm</u>
Aluminum (30)	Aluminum (30)	1.00
Aluminum (30)	Stainless Steel (30)	1.23
Stainless Steel (30)	Aluminum (30)	1.07
Stainless Steel (30)	Stainless Steel (30)	1.10
Stainless Steel (0)	Gold	0.68
Stainless Steel (0)	Stainless Steel (0)	1.53
Gold	Gold	0.405

(Electrode oxidation time - minutes is given in parentheses)

When results for the grouping of electrodes at the top of Table III are compared to those in Table II for liquid argon, it is apparent that similar sorts of reactive ratings are involved. Thus, cathode and anode effects like those in liquid argon must occur, also, in liquid methane even though it is a hydrocarbon liquid. The absolute values of electric strength for different liquids are not at all equivalent as shown in Table IV below.

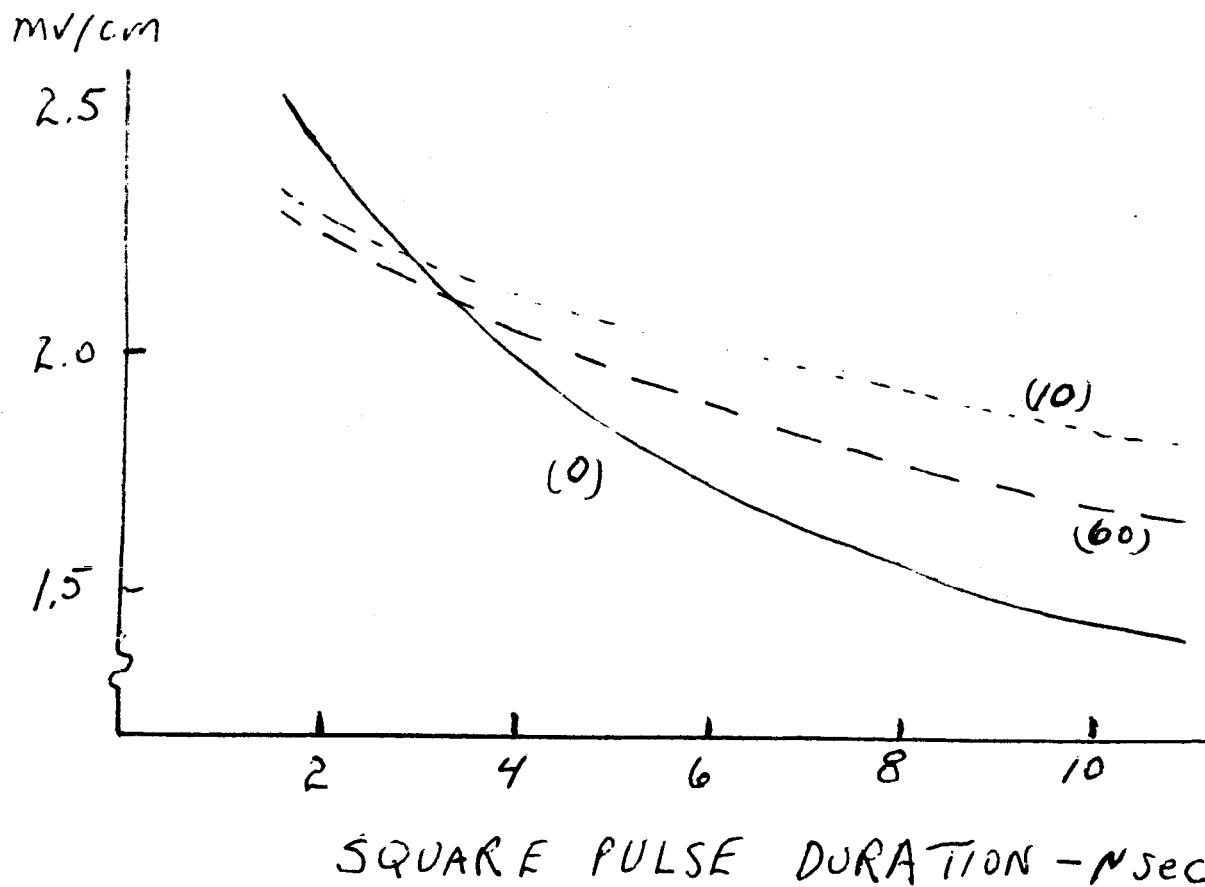


Figure 16. Electric Strength in Liquid Argon as a function of Pulse Duration Stainless Steel Electrodes -- Oxidized 0, 10 and 60 minutes as shown by values in ().

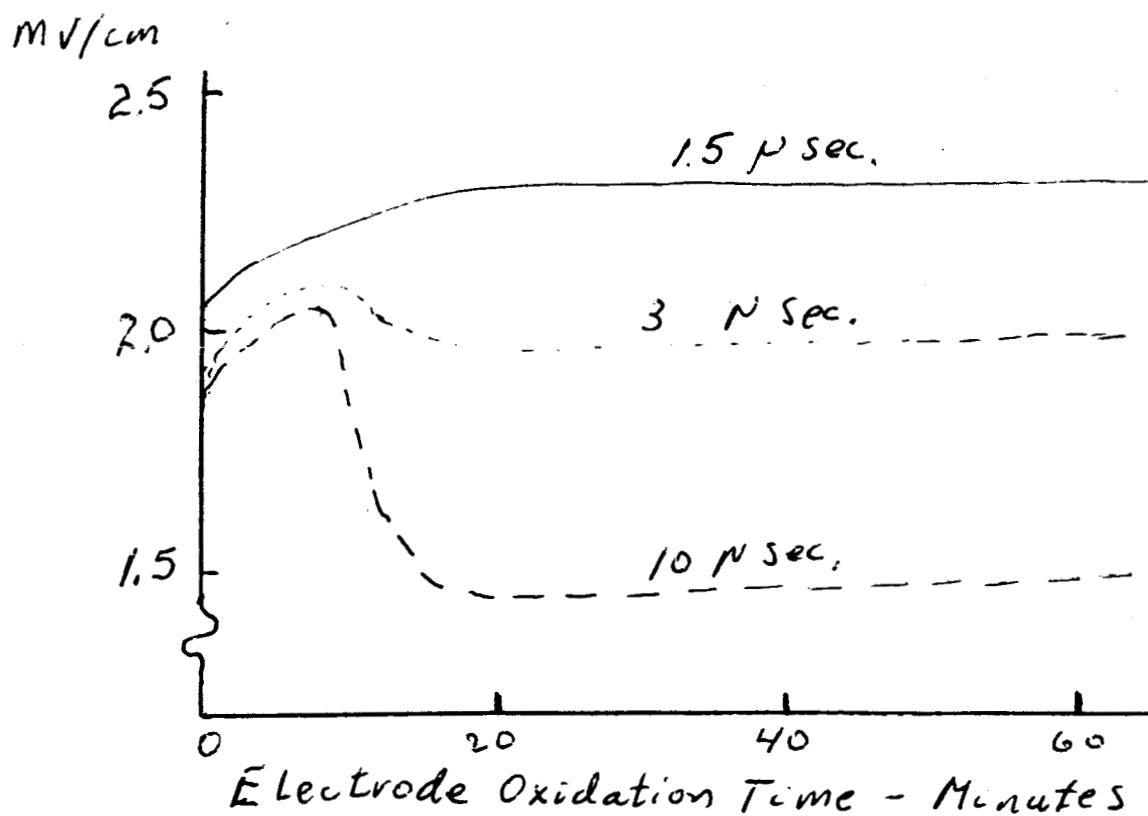


Figure 17. Electric Strength in Liquid Argon as a Function of Electrode Oxidation for Different Pulse Lengths. (Stainless Steel Electrodes)

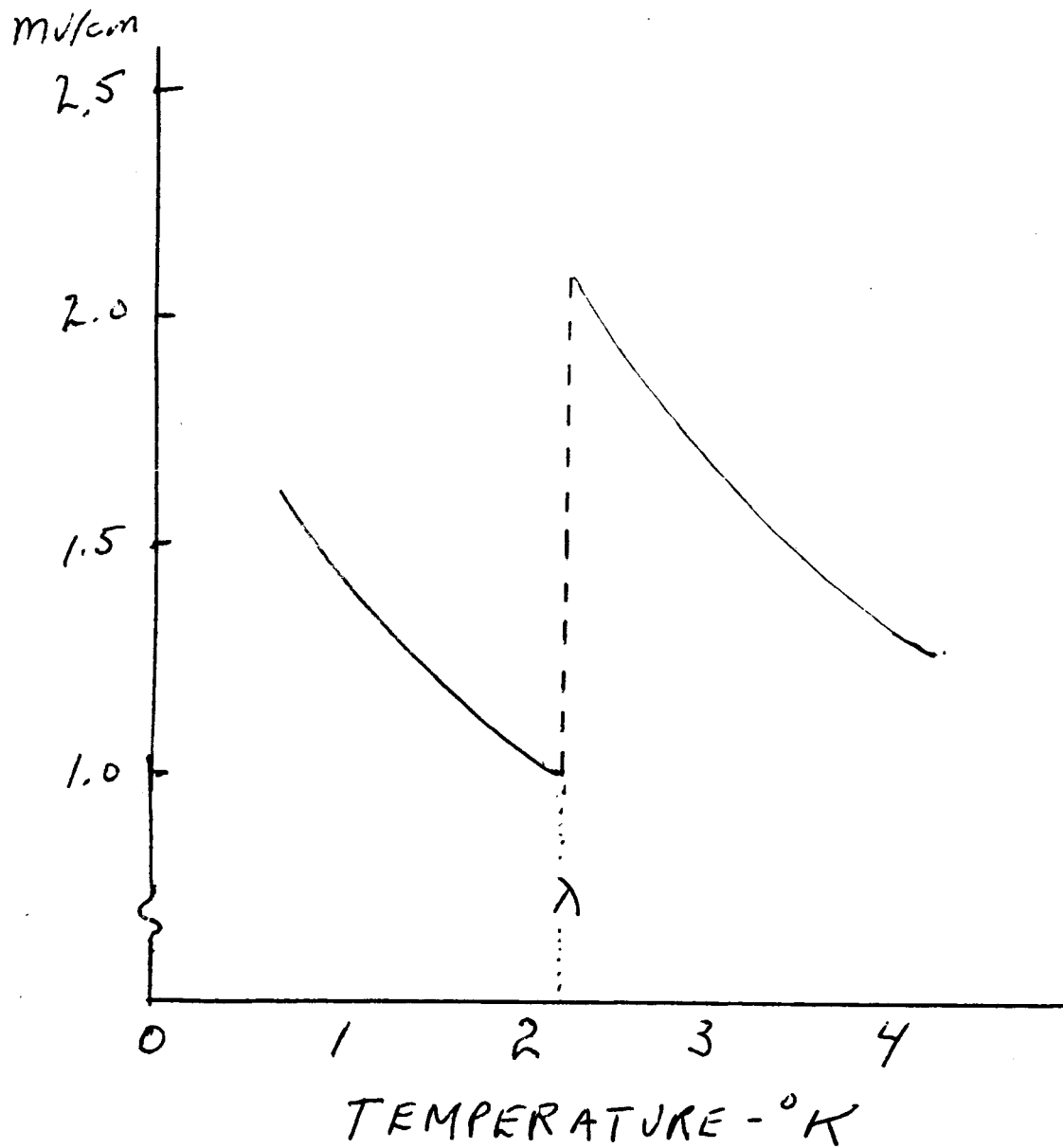


Figure 18. Electric Strength of Liquid Helium vs. Temperature Showing Critical Discontinuity at the λ Point.

TABLE IV

ELECTRIC STRENGTH AS A FUNCTION OF ELECTRODE MATERIAL (UNOXIDIZED)
COMPARISON OF DIFFERENT LIQUIDS AT THEIR BOILING POINTS

<u>Electrodes</u>	<u>Electric Strength, mv/cm</u>				
	<u>Methane</u>	<u>Argon</u>	<u>Oxygen</u>	<u>Nitrogen</u>	<u>Hexane* at 23 C</u>
Stainless Steel	1.53	1.40	2.38	1.88	1.4
Brass	0.84	1.01	1.44	1.62	--
Copper	1.375	1.40	1.81	--	--
Gold	0.405	1.16	1.24	1.50	--
Platinum	--	1.10	2.00	2.24	--
Aluminum	1.00	0.69	--	--	--

* The value for Hexane at room temperature was obtained in a similar fashion and is included for comparison. Many factors influence the breakdown voltage of hydrocarbons at room temperature and above.

It is interesting to note that the lowest breakdown is obtained with gold electrodes for Methane and with aluminum electrodes for Argon. It is important to recognize that the electrode material can influence the breakdown voltage of liquid methane by a factor of 3.8 to 1.

Unfortunately, the effect of electrode material does not appear to have been investigated in connection with the breakdown of liquid helium. However, Blank & Edwards (15) have measured the breakdown voltage of liquid helium over the temperature range of 1.2 to 4.2 K using polished steel electrodes with different configurations -- sphere to sphere, plane to plane, and point to plane. With point to plane electrodes they found breakdown voltages to be about twice as high with the point positive as compared with the point negative. It would appear that cathode emission is important.

Blank and Edwards found a higher value of electric strength at higher temperatures with a broad transition at the λ point. However, the electric strength also depends upon the gap spacing as shown in Figure 19. Unfortunately, the results with the small gap spacing are quite variable. At the larger gap spacings the values of electric strength are quite low -- generally lower than the lowest values found by Lewis with Argon for the worst electrode materials.

Blaisse and others (16) at Delft, Holland, have published a value of 0.7 Mv/cm* for liquid helium which is independent of temperature between 1.3 and 4.2 K. However, in conversation at Delft, Blaisse rejected his earlier work pointing out that the breakdown voltage of liquid helium is quite complex and very dependent upon purity of the liquid and character of the electrodes. For example, he has obtained values as high as 2.5 mV/cm in liquid helium both above and below the λ point.

* Spherical Tungsten anode and plane steel cathode.

(15) "Dielectric Breakdown of Liquid Helium", Blank & Edwards, Phys. Rev. Vol. 119, No. 1 (July 1, 1960) pp 50-52.

(16) Blaisse, van den Boogart & Erne, Bul. Inst. Int. Froid Annexe Vol. 1 (1958) p 333.

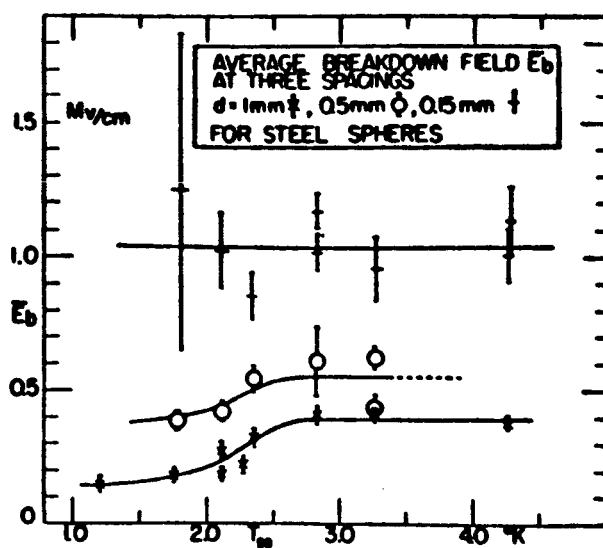


Figure 19. Average dielectric strength of liquid helium using steel spheres of diameter 9.52 mm, for three gap lengths, as a function temperature.

It is even more surprising that a sharp transition point occurs at the λ temperature as shown in Figure 18. (This figure has been taken from sketched notes and the absolute values are approximate.) At very small gap spacing there are indications that the effects shown in Figure 18 are reversed. The differences in breakdown above and below the λ temperature also are evident in the appearance of the steel cathode. Above the λ point the pitting produced by repeated breakdown is limited to a relatively small area on the surface. Below the λ point, the breakdown pits are small and spread out over the plane surface. Blaisse admits that work like that of Lewis should be undertaken with liquid helium also. He believes the theory of breakdown in helium to be more complex than that in Argon.

In reply to questions concerning breakdown in other simple, non-hydrocarbon liquids, Blaisse drew attention to the work of Young⁽¹⁷⁾ on liquid CO₂. Figure 20 gives results of breakdown measurements made on CO₂ at high pressure as the temperature was changed near the critical point of 31 C so that a transition occurred between the liquid and the gas phase. It is apparent that the electric strength also changed smoothly as a function of density without a marked discontinuity. Blaisse believes that similar effects would be found with liquid helium for which the critical temperature is 5.2 K and the critical pressure is 2.26 atmospheres. He has found in non-systematic work that the voltage breakdown of gaseous helium at the normal boiling point does not differ by a great deal from that of the liquid at the same temperature.

As mentioned earlier, no information seemed to be available on the electric strength of liquid hydrogen. Kok at Eindhoven believed he had a reference to liquid hydrogen in his new book⁽¹⁸⁾ but during the visit he could not find his own copy! (It has not been possible to find a copy so far in this country, either.) Kok is almost obsessed with the idea that colloidal particles dispersed in a liquid build "bridges" under electric stress which are primarily responsible for breakdown. He has developed the following expressions for liquid breakdown.

$$4\epsilon_0 \frac{\epsilon - \epsilon_0}{\epsilon + \epsilon_0} r^3 \epsilon_0^2 = KT$$

where ϵ - dielectric constant of the dispersed particle
 ϵ_0 - dielectric constant of the liquid
 r - diameter of the particle in Å

If $\epsilon \gg \epsilon_0$ then

$$4\epsilon_0 r^3 \epsilon_0^2 = KT$$

Using this last formula, he calculates particle sizes of 6 to 10 Å for the work of Lewis on the breakdown of cryogenic liquids. He attributes

(17) "Electric Breakdown in CO₂ from Low Pressures to the Liquid State", Young, J. of Appl. Phys. Vol. 21, (March 1950), pp 222-229.

(18) "Der Elektrische Durchschlag in Flüssiger Isolierstoffe", (Electrical Breakdown in Insulating Fluids), Kok, Contrex Verlag, Eindhoven, 1963.

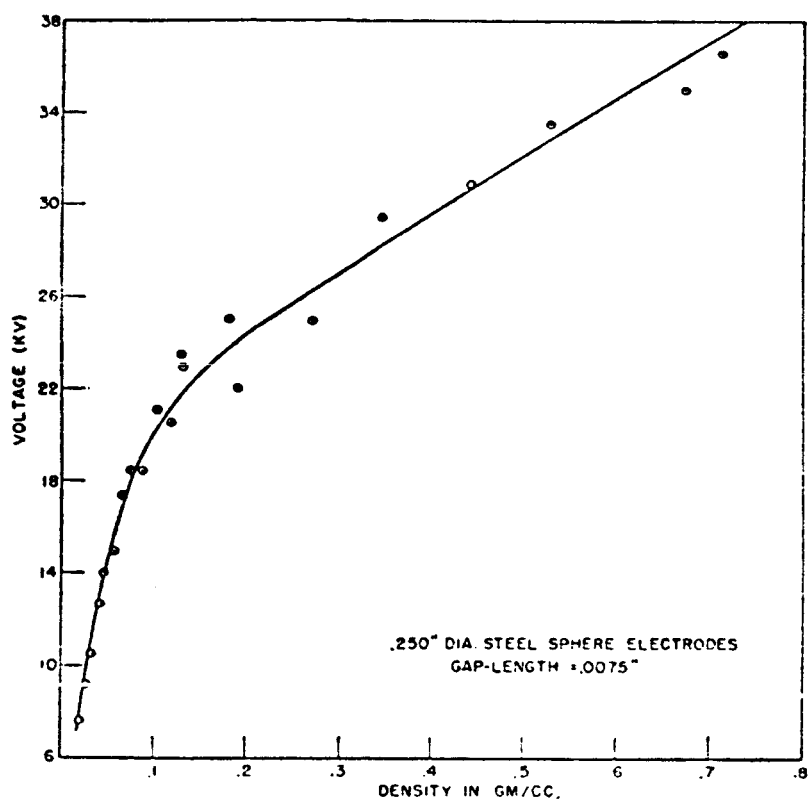


Figure 20. Breakdown voltage of CO₂ vs. density

these particles to fine residues of polishing compound on the electrodes. In addition, he has calculated particle size for breakdown in Blank and Edwards measurements arriving at 3 Å for 1.3 K and 6 Å for 4.2 K. He believes these calculated values are consistent with diameter of the caged ions in Careri's theory. It should be noted here that most investigators in the field do not appear to give much credence to Kok's proposals. They cannot be discounted entirely, however.

In final summary of the work on the breakdown of cryogenic liquids, it is obvious that a surprising amount of theoretical background is available primarily from the European investigators. Curiously, essentially no engineering attention has been paid to the same subject. The theoretical background does, of course, provide understanding of the relatively low 60 cps breakdown voltage of liquid helium found in the work under contract NAS8-2442. Electrode characteristics and the effect of purity should also be investigated with 60~ stress because of obvious practical implications. Moreover, high frequency breakdown of tests on cryogenic liquids should yield results of both practical and theoretical interest. With engineering application in mind, the very high values of electric strength for some cryogenic liquids may be most useful and believes the very low values might prove to be disastrous. As always, the best progress will be achieved with interplay between engineering and scientific investigation.

Capacitance and Loss

With the tremendous amount of theoretical interest in the electric strength of cryogenic liquids and the interest in ion mobility, it is amazing that practically no recent attempts have been made to measure the dielectric loss in cryogenic liquids. Kohler at Eindhoven, about 20 years ago, made a few scattered measurements and found the losses of cryogenic liquids to be too low to measure. He did develop a new precision bridge⁽¹⁹⁾ but apparently did not use it with cryogenic liquids.

Van Itterbeek⁽²⁰⁾ in Louvain, Belgium, recalled his measurements of the dielectric constants of liquid hydrogen and deuterium. He also attempted the measurement of loss but found it to be below the resolving capability of his bridge. His measurements were made at 530 KC with a vacuum capacitance of 20.25 $\mu\mu$ fd. and are summarized in the table below.

(19) "A New Alternating Current Bridge for Precision Measurements", Kohler & Koops, Phillips Res. Reports 1, pp 419-446 (Dec. 1940).

(20) "La Constante Diélectrique du Deutérium Liquide" (The Dielectric Constant of Liquid Deuterium), Van Itterbeek & Spaepen, Physica, Vol. IX, No. 3 (March 1942) pp 339-344.

<u>Liquid</u>	<u>p</u> <u>mm</u>	<u>T</u> <u>°K</u>	<u>e</u> <u>gr/cm³</u>	<u>ε</u>	<u>ε - 1</u> <u>ε + 2</u> <u>1</u> <u>e</u>
Deuterium	357	21.18	0.1685	1.272	0.494
	289	20.63	0.1698	1.275	0.494
	277	20.57	0.1699	1.275	0.494
	191	19.58	0.1722	1.277	0.491
	149	18.98	0.1735	1.281	0.494
	139	18.80	0.1739	1.282	0.492
Hydrogen	755	20.35	0.0709	1.226	0.988

Stewart⁽²¹⁾ has made dielectric measurements on liquid para-hydrogen over a temperature range of 24 to 100 K (2-320 atmospheres). He has found that the Clausius-Mosotti equation can be written as follows for liquid hydrogen.

$$C.M. = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{e} \text{ where } \frac{1}{C.M.} = 0.995823 - .090141e + 1.09896 e^2$$

Stewart's measurements were made primarily at 1 KC with some measurements at 10 KC for which the same results were obtained. He could not detect a measurable loss. It is interesting to extrapolate Stewart's data to the point given in Van Itterbeek's table above. Stewart's extrapolated value of CM = 992 compares well with the older value of 988. These values also compare very well with the data from contract NAS 8-2442.

Careri in Rome admitted that he had been tempted to measure dielectric loss in liquid helium containing γ radiation induced ions but so far had not made the attempt. In this situation the loss might be higher and measurable.

The extremely low dielectric losses and dielectric constants for many cryogenic liquids should also provide bases for engineering application.

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(21) Private Communication, Oct. 1, 1963 from Dr. John W. Stewart, Dept. of Physics, U. of Virginia, Charlottesville, Va.

ELECTRICAL PROPERTIES - NONMETALLIC MATERIALS
AT
CRYOGENIC TEMPERATURES

Very little, if any, work on electric strength of solids at cryogenic temperatures appears to be underway in European laboratories (or, for that matter, elsewhere in the world) at the present time. Limited DC Measurements have been made by Oakes⁽²²⁾ down to -196 C on several synthetic polymers primarily to investigate the so-called "intrinsic" breakdown. In very brief summary of this information, it may be stated that the "intrinsic" electric strength of crystalline polymers, such as polyethylene, increases with decrease in temperature below room temperature and that for non-crystalline polymers remains relatively constant.

Several European laboratories are studying the dielectric constant and the dielectric loss index (factor) of polymeric materials over a range of frequency and temperature. In particular, Reddish in England, as well as Thurn and Wurstlin at BASF in Germany have carried such measurements to low temperatures. Generally, dielectric properties at very low temperatures have not been investigated. Much of this work has been limited to lower temperatures of about -80 probably because the maxima in the dielectric loss usually occurs above this temperature. Thurn and Wurstlin⁽²³⁾ have plotted the temperature of these maxima as a function of frequency as shown in Figure 20. Langbein⁽²⁴⁾ has summarized many of these studies. During a visit to the Deutschen Kunststoff-Institut in Darmstadt, Langbein described some of his own unpublished dielectric measurements at temperatures down to -160 C. He is looking for proton jumps in the H₂ bridges and for rotation in carbonyl groups, particularly in aliphatic polyesters. A β transition has been found in these polymers as low as -160 C. Effect of molecular weight is being studied and correlary work on near infrared absorption is underway. Langbein used dielectric techniques to follow crystalline growth in polymers at temperatures as low as -80 C. He mentioned similar work at BASF in Ludwigshaven at -100 C.

The Russians, also, appear to be making dielectric loss measurements down to at least liquid nitrogen temperatures according to Russian representatives to the IEC Meeting in Venice. They mentioned only one reference with which we were already familiar.⁽²⁵⁾ The Russian work describes some surprising dielectric loss peaks at low temperatures (i.e., polytetrafluoroethylene). The peak for polytetrafluoroethylene has been confirmed by McMahon at DuPont who has found another peak at lower temperatures with polyperfluoroethylene-propylene. Obviously much can be learned about polymer structure with dielectric measurements at low temperatures.

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- (22) "The Intrinsic Electric Strength of Polythene and its Variation with Temperature", Oakes, J. IEE, (1948), Vol. 95, Pt 1, p 36
"The Electric Strength of Some Synthetic Polymers", Oakes, Proc. IEE Pt. I, Vol. 96, (1949), p 37.
- (23) Thurn & Wurstlin, Kolloid- Z, Vol. 145 (1956).
- (24) "Die Anwendung der dielectricischen Methode bei der Untersuchung von Kunststoffen", (The Use of Dielectric Methods in Research on Plastics), Langbein, Kunststoffe, Vol. 9, (January 1961) pp 503-508.
- (25) "The Electrical Properties of Polymeric Insulation", in Russuan, Milcailov & Sazhin, Uspelchi Khimii, Vol. 29, No. 7 (1960) pp 864-881.

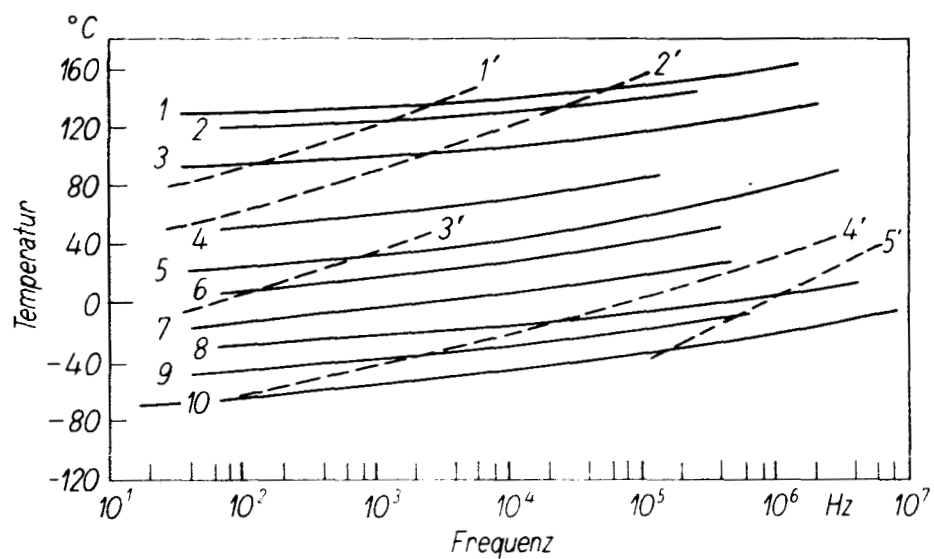


Figure 21. Temperature-Frequency Shift for the Dielectric Loss Maxima of Different Polymeric Materials

———— Principal maxima - - - - - Adjoining maxima

Principal maxima

1. Rubber with 32% Sulfur
2. Polyvinylformal
3. Polyvinylchloride
4. Polyvinyl-2 ethylhexanol
5. Polyvinylpsopronate
6. Rubber with 12% sulfur
7. Rubber with 8% sulfur
8. Rubber with 4% sulfur
9. Rubber with 0% sulfur
10. Glycerin

Secondary maxima

- 1' x-cloromethylester of poly-methylacrylic) acid
- 2' Polymethylmethacrylate
- 3' Polyvinylchloride
- 4' Polyethyleneterephthalate
- 5' Cellophane

Volger in Eindhoven mentioned the fundamental work of M. Freymann and R. Freymann in Paris on the dielectric properties of some inorganic and also non-polymeric organic compounds which extends to very low temperatures. The Freymanns have recently published a very interesting summary of this work.⁽²⁶⁾ Figure 22, taken from this work, illustrates the very complex and as yet unexplained, multiple absorption peaks which occur with Thiophene at very low temperatures. With the exception of Thiophene, dielectric absorption at low temperatures in simple organic compounds has been separated into two classes:

1. Strong dipolar absorption for super-cooled state
2. Weak dipolar absorption from
 - a. Rotation of groups in the molecule in the solid state
 - b. Presence of traces of uncrystallized (supercooled) pure material
 - c. Presence of a liquid or supercooled liquid impurity
 - d. Presence of a solid impurity (lattice defect).

Jaffrain, a colleague of the Freymanns, has extended the study of 37 organic compounds.⁽²⁷⁾ He has studied frozen solutions of some of these compounds in carbon tetrachloride and chloroform. Compounds, which in the pure form exhibit weak dipolar absorption, may show strong absorption in solution. The study of solutions permits the deterioration of relationship between the eutectic point, the phase transitions and the dipolar absorption. Reference should be made to the paper for detailed discussion of these inter-relationships.

Volger and Stevels⁽²⁸⁾ have found interesting dielectric absorption peaks at low temperatures in fused silica (silica glass) and many types of glass. Typical results are shown for fused silica in Figure 23; temperature quenched, fused silica in Figure 24; and for temperature stabilized lead glass in Figure 25. However, unlike crystalline quartz to be discussed later, the dielectric properties of the glasses at low temperature are unaffected by γ irradiation even though the glasses become colored. At higher temperatures, irradiation does decrease the dissipation factor of silica glass with small additions of alkali oxide as shown in Figure 26, but does not affect the properties of pure fused silica. The low temperature dielectric losses in glass are probably dependent primarily on relaxation mechanisms. The relaxations appear to involve rather complex network vibrations and the influence of network defects on them. Volger believes that ion migration losses, which are present in glass at room temperature, disappear at very cold temperatures.

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(26) "A Contribution to the Study of the Dielectric Properties of Organic Compounds", Freymann & Freymann, Dielectrics, Vol. 1, No. 2 (May 1963) pp 98-102.

(27) "Debye Dipolar Absorption and Phase Transitions in Frozen Organic Liquid Compounds with One (or More) C = O Groups", Jaffrain, Dielectrics, Vol. 1, No. 2, (May 1963) pp 103-109.

(28) "Further Experimental Investigation of the Dielectric Losses of Various Glasses at Low Temperatures", Volger & Stevels, Philips Res. Rep., Vol. 11, (1956) pp 452-470.

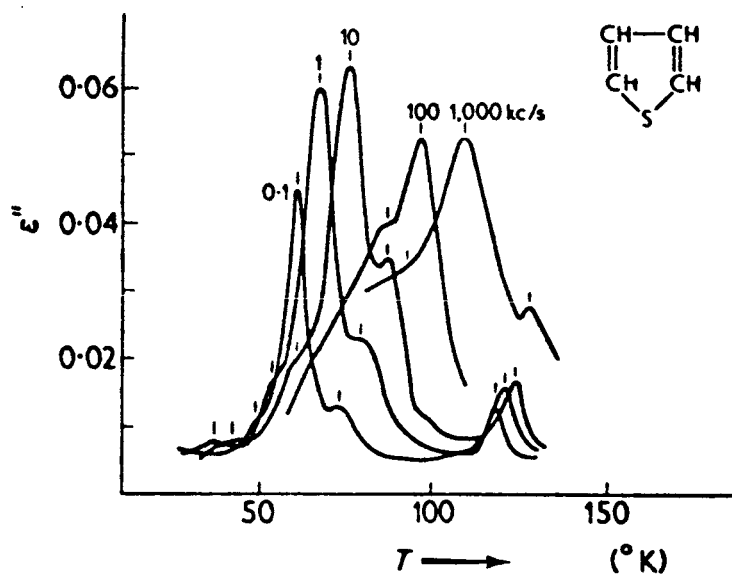


Figure 22. Thiophene

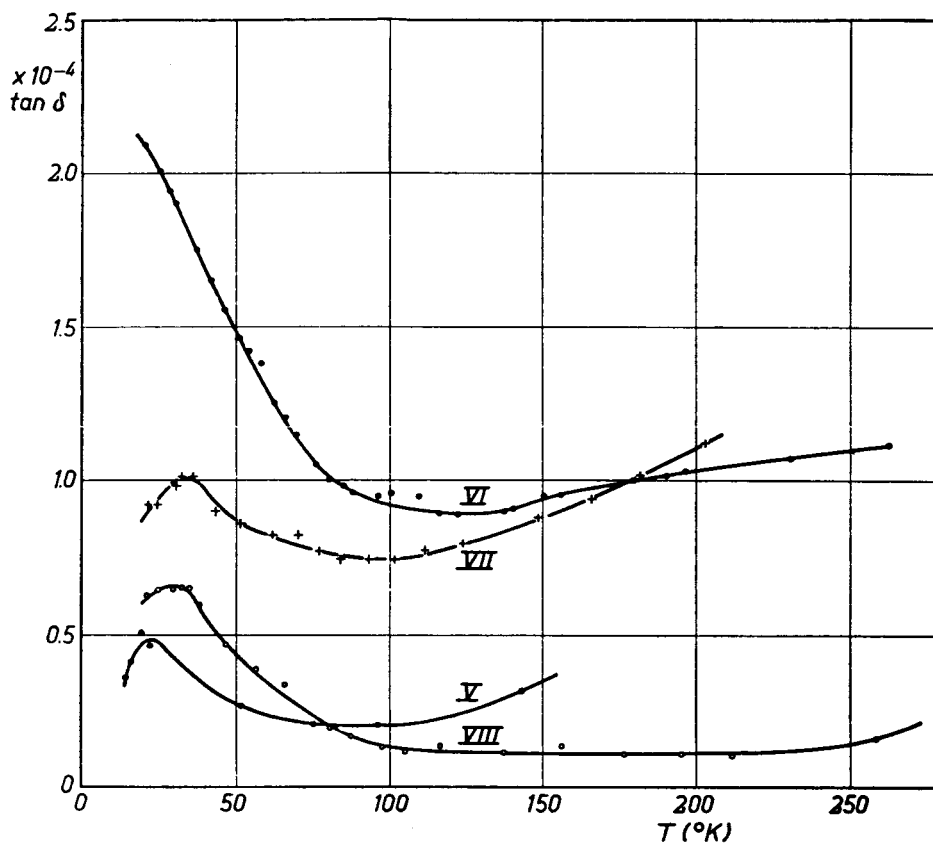


Figure 23. $\tan \delta$ vs. T of four samples of fused silica, measured at 32 kc/s.

- Curve V : fused silica with 0.5 mole % of Al_2O_3 .
- Curve VI : "Corning" fused silica, aluminium-free.
- Curve VII : "G.E.C. (U.S.A.)" fused silica, containing no water
- Curve VIII: "G.E.C. (U.S.A.)" fused silica, containing some water.

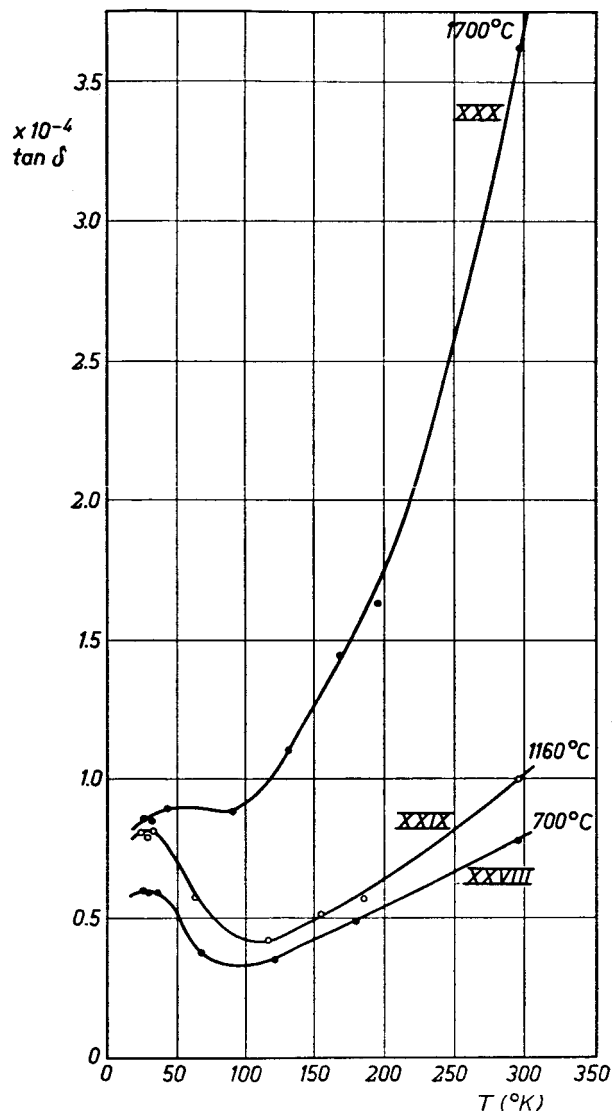


Figure 24. $\tan \delta$ vs. T of three samples of fused silica quenched from the temperatures indicated. Measuring frequency 1 kc/s.

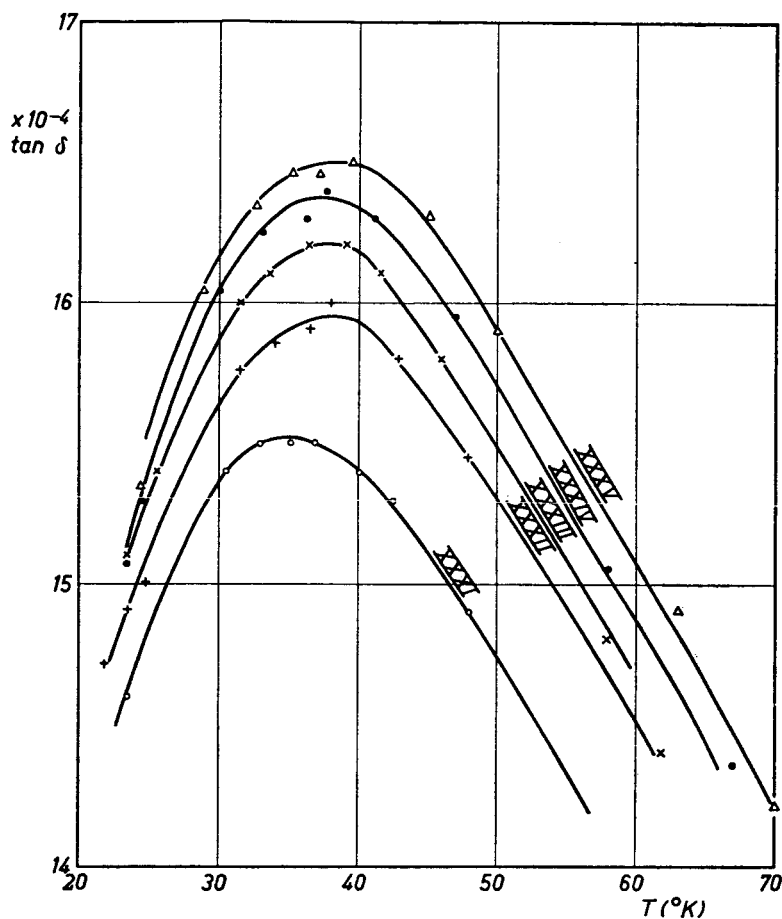


Figure 25. $\tan \delta$ vs. T of samples of a lead-silicate glass, stabilized at different temperatures. Measuring frequency 1 kc/s. Composition of the glass in weight percentages: 56.2 SiO_2 ; 7.6 Na_2O ; 4.5 K_2O ; 30.0 PbO ; 1.2 Al_2O_3 ; 0.3 Sb_2O_3 ; 0.25 MnO .

Curve XXXI :	stabilized at 400°C .	Curve XXXIV:	stabilized at 440°C .
Curve XXXII :	" " 420°C .	Curve XXXV :	" " 450°C .
Curve XXXIII:	" " 430°C .		

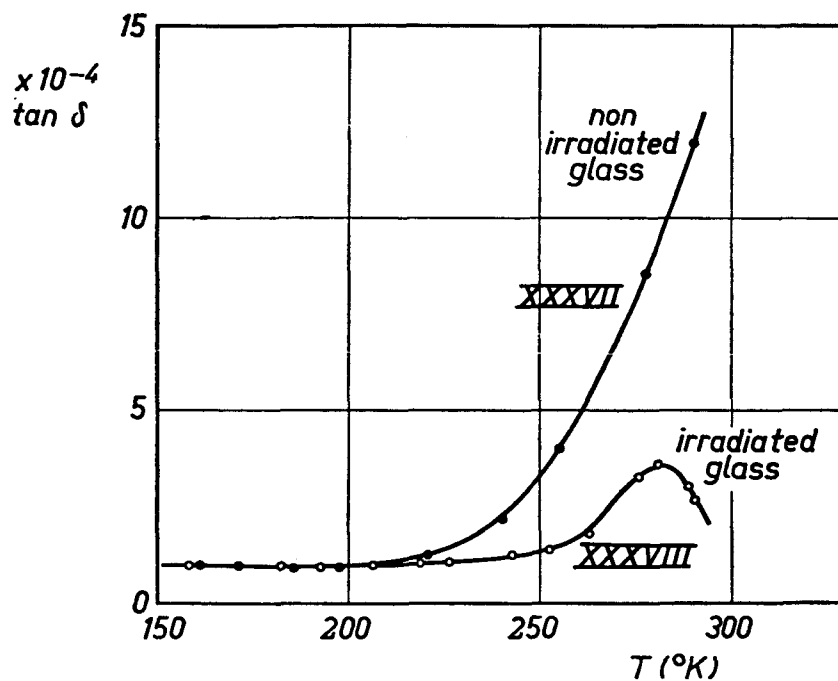


Figure 26. Influence of 3.10^6 r of 450-kV X-rays upon the power factor of a glass specimen containing 99 mole % SiO_2 and 1 mole % BaO . Measuring frequency 32 kc/s. Similar curves have been obtained with glasses containing 99 mole % SiO_2 and 1 mole % Na_2O or Cs_2O .

Stevell and Volger⁽²⁹⁾ have extended their low temperatures studies to include crystalline quartz. In "clear" quartz, three dielectric loss maxima occur in "virgin" quartz as shown in Figure 27. Irradiation induces new absorption peaks (at different temperatures) and diminishes or ultimately eliminates the naturally occurring peaks. "Bleaching" at 300 C only slightly decreases the size of the peak in this case. Volger attributes the peaks to "color centers" even for clear quartz crystal. All sorts of irradiation -- even ultraviolet -- produce color centers and in turn produce dielectric loss peaks in quartz. It is most interesting that radiation may also introduce new loss peaks (at a different temperature) in natural quartz crystal but merely amplifies the same peak in synthetic crystal.

Color centers in colored quartz crystals give relatively high loss peaks at low temperatures as shown in Figure 28. The effect of thermal bleaching in reducing the dissipation factor peak is marked. The intensity of bleaching in Figure 28 is as follows:

1. Virgin smoky quartz crystal of Ukrainian origin
2. A few hours at 300°C
3. Prolonged exposure at 300°C
4. A few hours at 400°C
5. Twenty hours at 550°C.

At 400 and particularly 500 C new peaks are introduced. It is interesting to note how closely the shape of curve S in Figure 28 compares to the shape of the curve for virgin "clear" quartz crystal in Figure 27. Obviously curves of $\tan \delta$ at different frequencies provide important information as shown in Figure 29. It is interesting that the peak becomes quite broad when plotted as a function of frequency at 16°K (Figure 30). Considerably more experimental information is given in Volger's paper and reference should be made to it for the details. He is able to identify the various kinds of ions by the temperature at which peaks occur with a measuring frequency of 32 kc/s as tabulated below.

<u>Ion</u>	<u>Temperature of Dielectric Loss Peak</u>
Lithium	60°K
Sodium	38 and 95°K
Potassium	140°K
Silver +	22°K
Copper +	225°K

Volger extends his theoretical discussion to the way in which ions enter into the crystal lattice, the influence of impurities the aluminum, the vibrational modes, etc. More detailed discussion does not seem merited here and for details reference should be made to the paper. In conversation at Eindhoven, Volger indicated that he is extending his theoretical investigation even further utilizing the "poloren" theory first suggested by Fröhlich and expanded by Holstein in the U.S.A. and Sewell in England. In summary, it is interesting to see how dielectric measurements at

 (29) "Further Experimental Investigations on the Dielectric Losses of Quartz Crystals in Relation to Their Imperfections", Stevells and Volger, Philips Res. Repts. Vol. 17 (1962) pp 283-314.

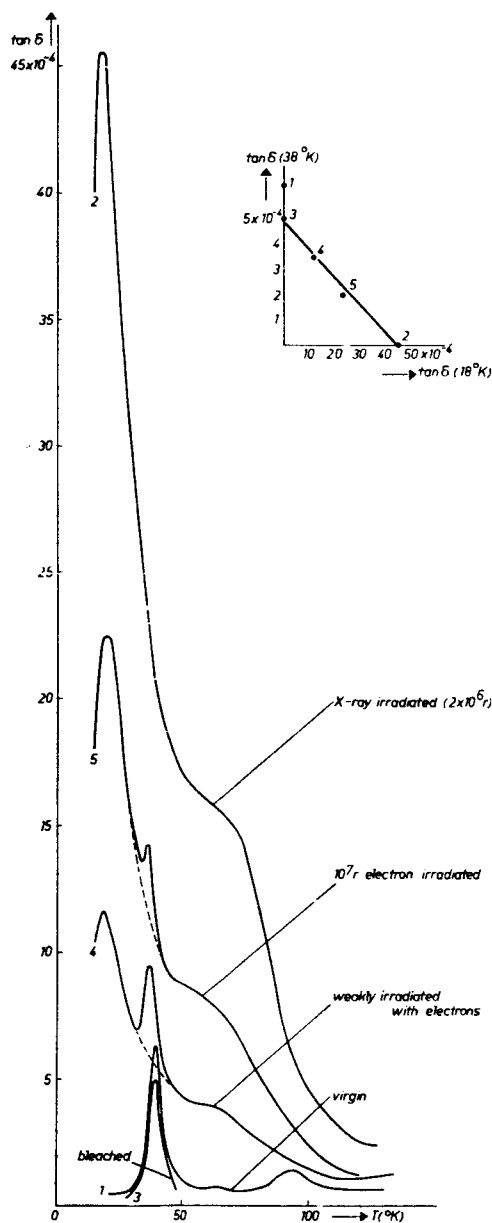


Figure 27. $\tan \delta$ vs. T curves for a synthetic quartz crystal, C4, measured at 32 kc/s. Part of the data in this figure can also be found in Fig. 5 of an earlier paper. The insert shows the relation between the peak heights, at 18 and 38°K respectively, which are supposed to be proportional to the concentration of colour centres and progenitors.

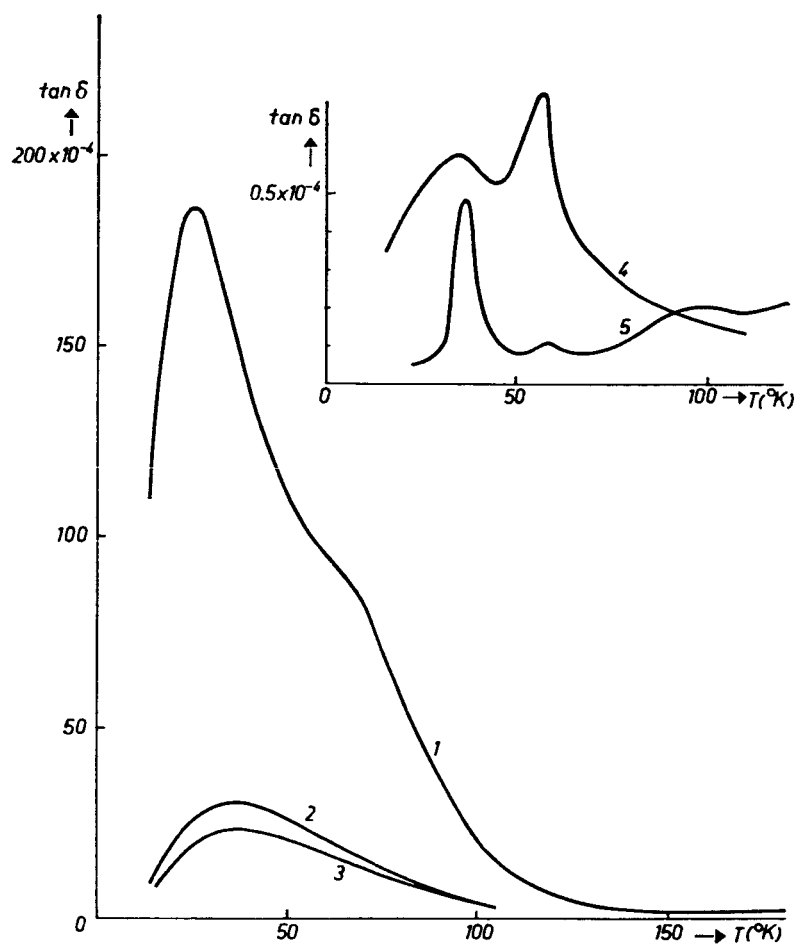


Figure 28. $\tan \delta$ vs. T curves for a natural smoky quartz crystal, C19, in different stages of bleaching. Measuring frequency 32 kc/s.

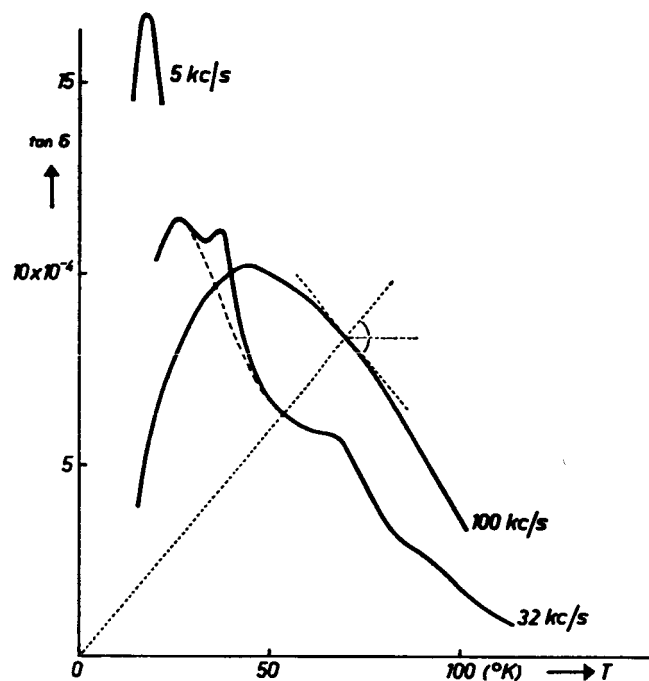


Figure 29. $\tan \delta$ vs. T curves taken at three different frequencies on an X-irradiated synthetic crystal, C11. This crystal contains 0.02% Ge. See Fig. 30.

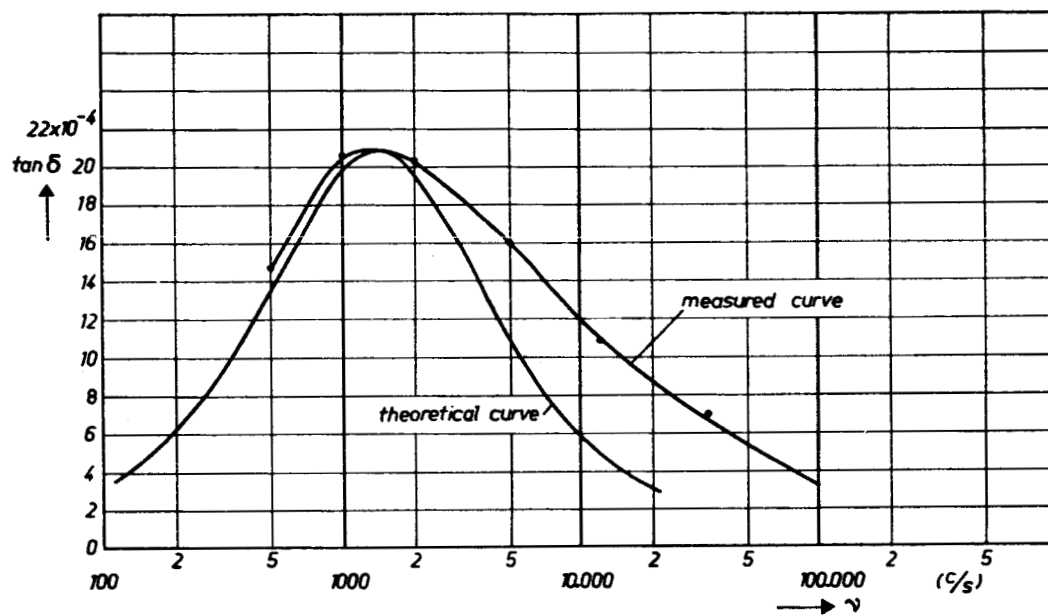


Figure 30. $\tan \delta$ vs. ν curve, taken at 16°K on an X-irradiated synthetic crystal, C11. See Fig. 29.

cryogenic temperatures can be used to "fingerprint" ionic impurities in crystal lattices and to develop fundamental understanding of crystal structure.

Volger mentioned, but did not describe, other work with dielectric measurements at cryogenic temperatures on semi-conductors (i.e., Fe_2O_3 doped with Lithium). Occasional reference can be found also in the literature to dielectric measurements on ferroelectric materials at cryogenic temperature. In example, (30) dielectric measurements have been made on ceramic barium titanate at temperatures from 2.8 to 298°K with frequencies from 500 KC to 2 mc. A typical curve from reference 30 is shown in Figure 31. The peak in the dielectric constant at 280°K is attributed possibly to change in domain size and should not be confused with the larger peak at 393 K where there is a change in structure. The broad peak in $\tan \delta$ (dotted curve) just below 100°K and the steady decrease of the dielectric constant at temperatures below about 200 C is characteristic in this author's opinion of a dipole loss. However, Blunt and Love found no frequency dependence over the entire temperature range. (Note: This author has found a similar lack of frequency dependency for titanates at cryogenic temperatures but did find some frequency dependency at room temperature.) Thus, no theoretical explanation can be advanced for the broad low temperature dissipation factor peak and the large decrease in ϵ' as the temperature is decreased. It can be assumed, of course, that the binding of the titanium ion increases as the temperature increases. (Loose binding of the titanium in the crystal unit is generally believed to contribute high ϵ' at normal temperatures.) This explanation is difficult to accept in view of the lack of frequency dependency. From the practical point of view, it should be noted that in addition to a very large decrease in dielectric constant, the dissipation factor is .0108 at 2.8°K which is considerably higher than the value of .00347 at 24°C. In contrast to the casual opinion of the uninformed, dielectric loss does not necessarily decrease to very low values at cryogenic temperatures.

PHYSICAL PROPERTIES OF NONMETALLIC MATERIALS AT CRYOGENIC TEMPERATURES

In general, much more attention has been paid to physical than to the electrical properties of plastics, ceramics and other non-metallic materials at low temperatures. As for electrical properties, the physical properties at low temperature are often incidental to measurements at higher temperatures. Consequently, it is difficult to find co-ordinated studies at low temperatures. For the purpose of this report, specific comment will be made in a few areas and a more extensive list of references will be appended.

In Europe, most investigations of physical properties at low temperatures have been conducted primarily with theoretical considerations in mind. Perhaps for this reason, great emphasis has been placed on

- (30) "The Dielectric Properties of Barium Titanate at Low Temperatures", Blunt & Love, Phys. Rev., Vol. 76 No. 8 (Octo. 15, 1949) pp 1202-1204.

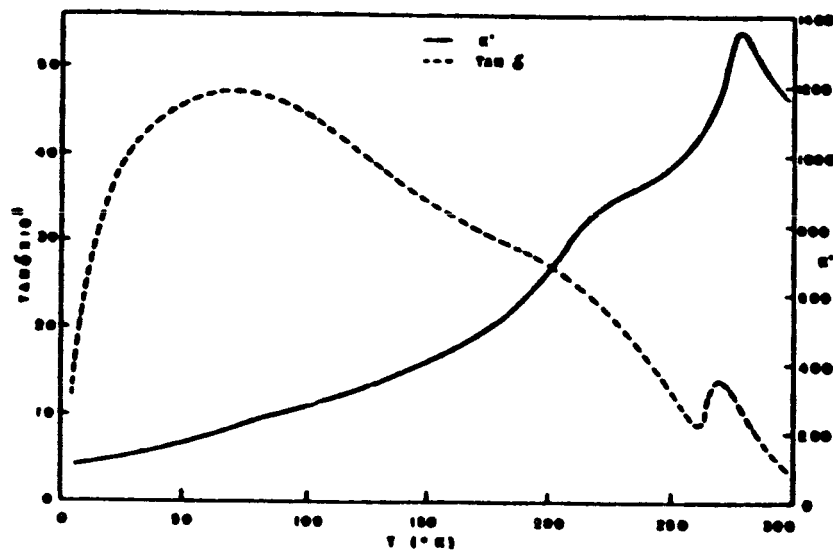


Figure 31. K' and $\tan \delta$ of BaTiO_3 versus temperature.

thermal conductivity measurements since thermal conductivity is influenced by so many factors related to the physical state. It must be remembered, also, that some physical measurements (i.e., tensile strength and elongation) may be relatively difficult to make at low temperatures. In consequence, data in these experimentally difficult areas may be scarce. In the following, physical properties will be discussed under several headings.

LINEAR AND VOLUME CONTRACTION

Many measurements of dimensional change with temperature change have been reported and no attempt will be made to cover such work. Instead, a few references to several "off-beat" studies will be made including optical methods for measurement.

Hellwege⁽³¹⁾ et al at Darmstadt have measured thermal contraction to -80 C for polyvinylchloride which had been prestretched by various amounts as shown in Figure 32. That such anisotropy extends to low temperatures is surprising. Knappe⁽³²⁾ has pointed out how compressive stresses can develop the surface of a thick plate of polymethylmethacrylate exposed at low temperatures as shown in Figure 33. Knappe also describes surface failures in polystyrene after exposure in liquid nitrogen.

The difficulties in making accurate linear contraction measurements at very low temperatures are obvious. Blaisse⁽³³⁾ at Delft and others have used interferometer techniques particularly for studying quartz. Deflection of light in a prism of solid argon⁽³⁴⁾ has been used also as an ingenious and very accurate method for determining the coefficient of thermal expansion for solid argon.

THERMAL CONDUCTIVITY

Great emphasis seems to have been placed on thermal conductivity over a wide range of temperatures. In particular, Hellwege and others at the Deutschen Kunststoff-Institut, Powell and others at the National Physical Labs in Teddington and Glen Stack at the G.E. Research Lab. in Schenectady have made contributions to these studies. A list of references in this area is appended. From the theoretical point of view, in non-conductors thermal energy is carried primarily by phonons. A phonon may be described as a normal mode, elastic

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- (31) "Anisotropic der Wärmeausdehnung und Wärmeleitung in einachsigen verestreckten amorphen Hochpolymeren", (Anisotropy in Expansion and Thermal Conductivity in Unidirectional, Pre-stretched Amorphous High Polymers), Hellwege, Hennig & Knappe, Kolloid-Z, Vol. 188, No. 2, pp 121-127 (1963).
 - (32) "Die Festigkeit thermoplastischer Kunststoffe in Abhängigkeit von den Verarbeitungsbedingungen", (The Strength of Thermoplastics as a Function of Service Conditions), Knappe, Kunststoffe, Vol. 51, No. 9, (1961) pp 562-569.
 - (33) "Thermal Expansion Coefficient, Refractive Index and Double Refraction of Crystalline Quartz between 4 and 270°K", Lebesque, Blaisse & Scheele, Inst. Int. du Froid, Annexe 1960-1, pp 265-271.
 - (34) "Optical Determination of the Compressibility of Solid Argon", Smith & Pings, J. Chem. Phys., Vol. 38, No. 4, 15 Jan. 63, pp 825-827.

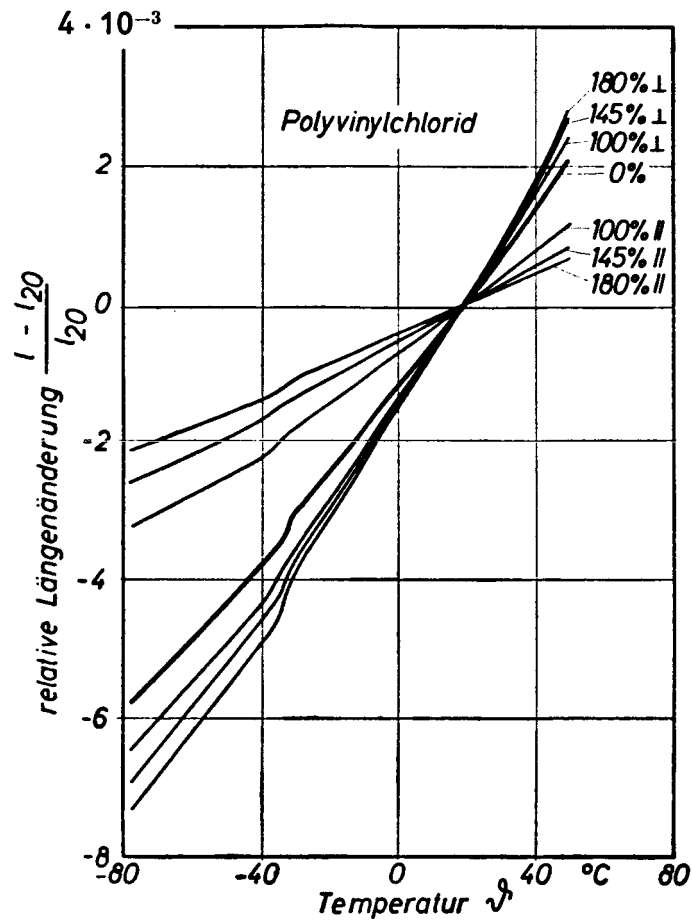


Figure 32. Relative Change in Length of PVC versus Temperature for Different Degrees of Pre-stretching both Horizontal and Vertical to the Change in Length.

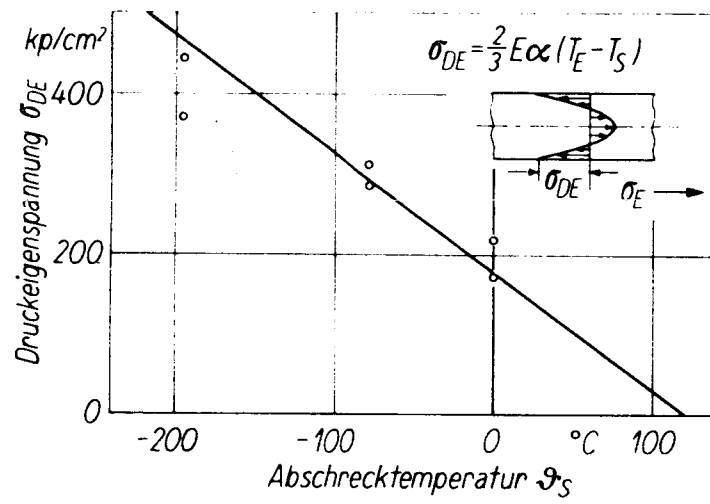


Figure 33. Compressive Stresses in the Surface of Polymethylmethacrylate Plates versus the Stressing Temperature

vibration of the crystal lattice (or molecular order) that possesses a definite frequency and a quantum of energy. Obviously, phonon migration will be subject to physical factors and other effects in the material. Some of these effects may be pronounced -- others secondary. At any rate, thermal and electrical conductivity depend on quite different mechanism so thermal conductivity measurements may be sensitive in areas where dielectric measurements are not.

Eiermann and Hellwege⁽³⁵⁾ have reviewed the thermal conductivity of high polymers from -180 C to 90 C. Some of the more interesting curves are reproduced here. Anisotropy in the thermal conductivity of polymethylmethacrylate can be induced by stretching the polymer as shown in Figure 34. Three kinds of performance occur in partially crystalline polymers as shown in Figure 35. No theoretical information can be advanced to explain the slight and broad peak for high pressure polyethylene and why thermal conductivity of polychlorotrifluoroethylene increases slightly with increase in temperature and that for high pressure polyethylene decreases. It is reasonable to assume that a larger number of energy transitions must take place between the shorter molecules in high pressure polyethylene as compared to low pressure polyethylene with its higher molecular weight. Thus, the relative magnitudes of the thermal conductivity can be rather generally explained but not the change of conductivity with change of temperature. Finally, the second order transitions do show as breaks in thermal conductivity curves as could be expected. (Figure 36) The small variations in the curve for polytetrafluoroethylene (Teflon) are interesting but are not commented on by the author. It is this author's opinion that the variations may indicate some of the weak transformations known to exist in TFE in addition to the strong second-order transition at about 20 C. Because of its practical importance, curves for plasticized PVC are plotted in Figure 37. The transition temperatures decrease with increased plasticizer content as would be expected. It would be most interesting to compare the transition temperatures for thermal conductivity as compared to those measured with vibrational mechanical and electrical stress.

Several other references to thermal conductivity have been placed in the appended bibliography.

MECHANICAL RELAXATION

As for dielectric processes, an enormous number of investigations have been made of mechanical relaxation at normal and elevated temperatures but relatively few of these investigations have been carried to very low temperatures. Wolf of BASF in Ludwigshaven has shown data at low temperatures in his review⁽³⁶⁾ of the subject. A typical example showing the marked difference between linear and branched polyethylene is reproduced in Figure 38. The original reference and its bibliography can be consulted for many other interesting examples. Again, this author must point out the additional information which could be gained from a coordinated comparison of the absorption peaks from mechanical and electrical data with the transition in thermal conductivity.

(35) "Thermal Conductivity of High Polymers from -180°C to 90°C",

Eiermann and Hellwege, J. of Polymer Sci., Vol. 57 (1962) pp 99-106

(36) "Relaxationsuntersuchungen zum Studium der molekularen Vorgänge in Hochpolymeren" (Relaxation Investigations in the Study of Mechanical Processes in High Polymers), Wolfe, Zeitschrift für Elektrochemie, Bd. 65, Nr. 7/8, 1961.

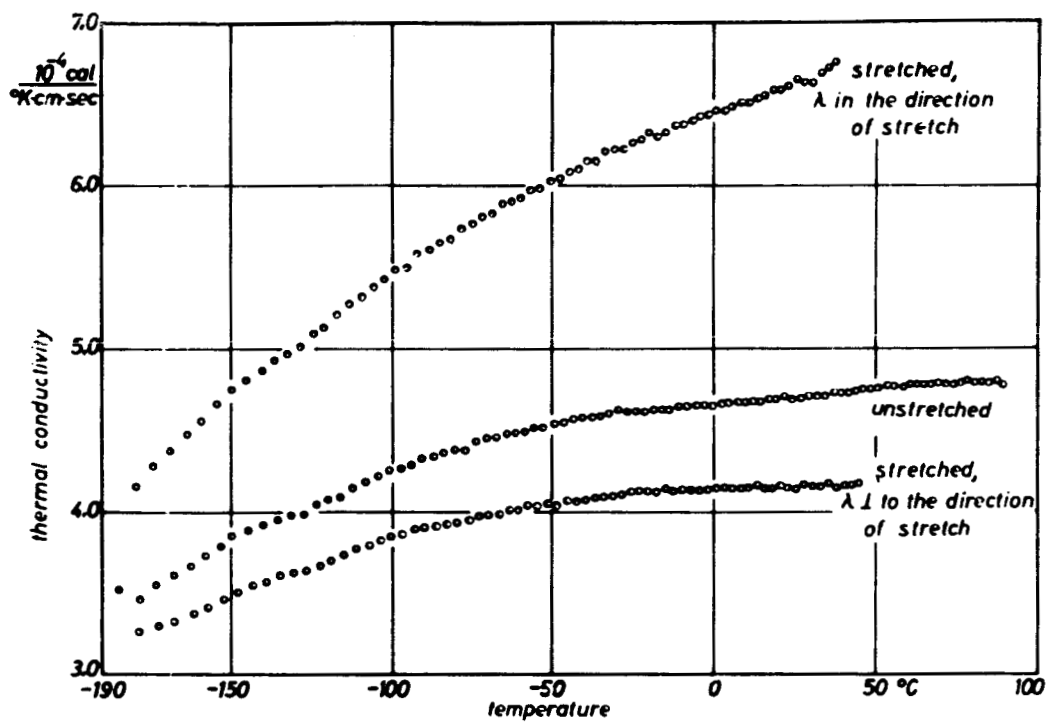


Figure 34. Thermal Conductivity of Polymethyl Methacrylate: Unstretched and Stretched to 375%.

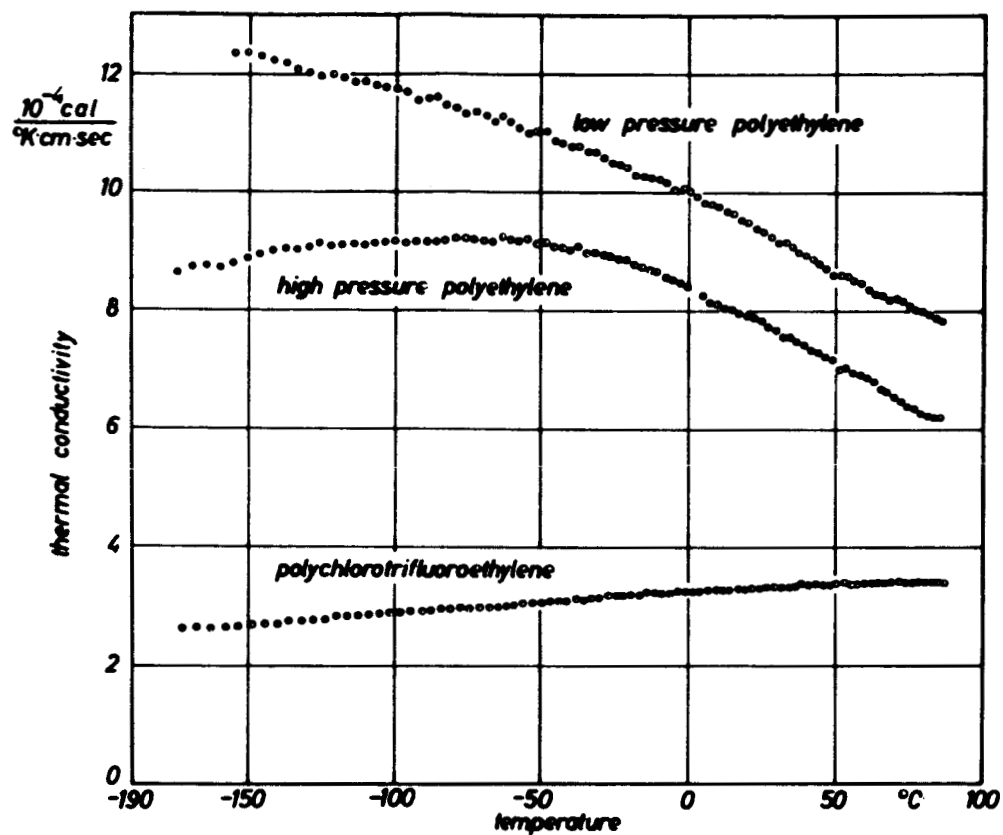


Figure 35. Thermal Conductivity of Polyethylene and Polychlorotrifluorethylene.

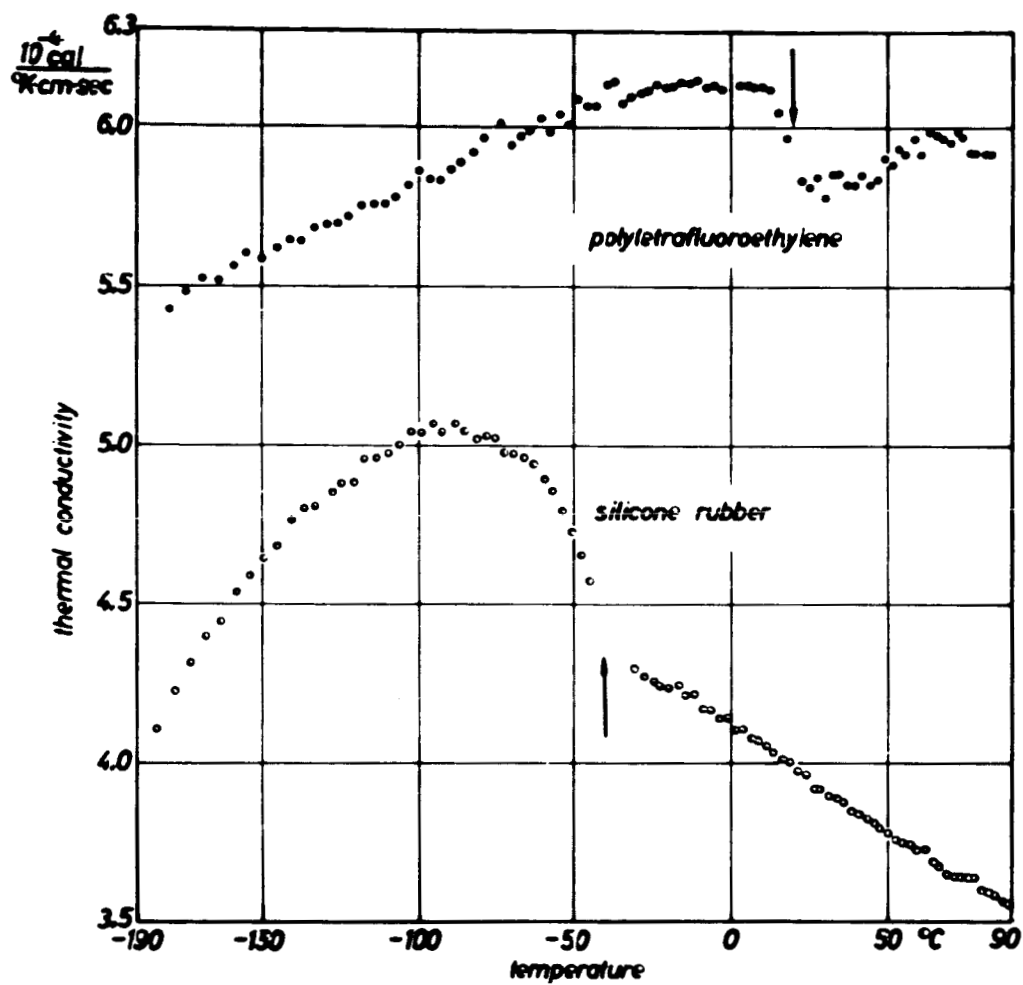


Figure 36. Thermal Conductivity of Polytetrafluoroethylene and Silicone Rubber.

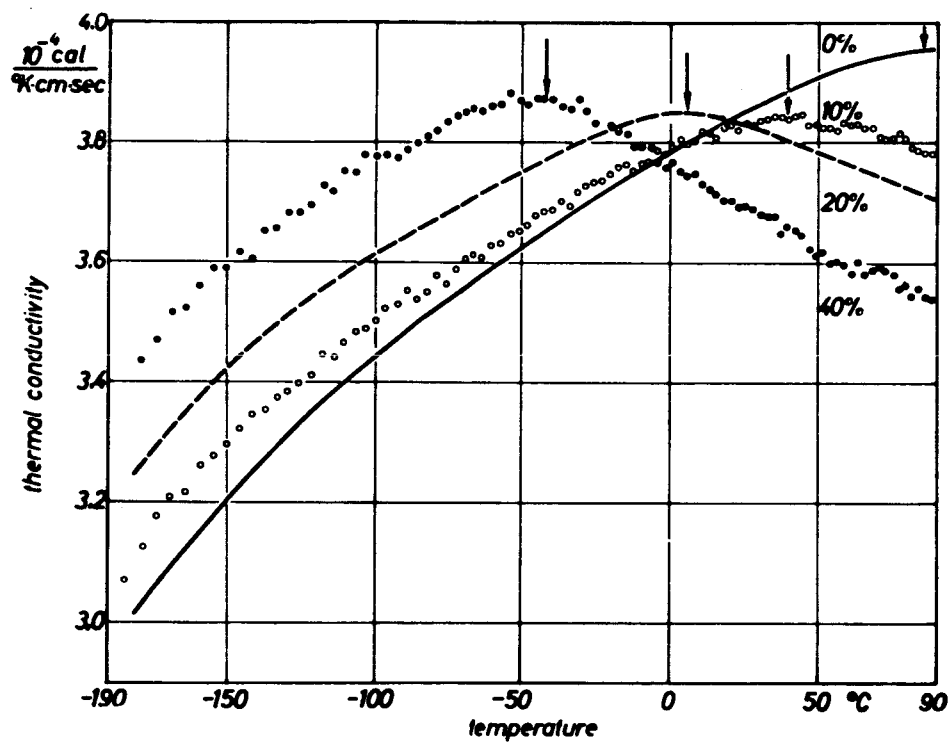


Figure 37. Thermal conductivity of polyvinyl chloride with different plasticizer contents.

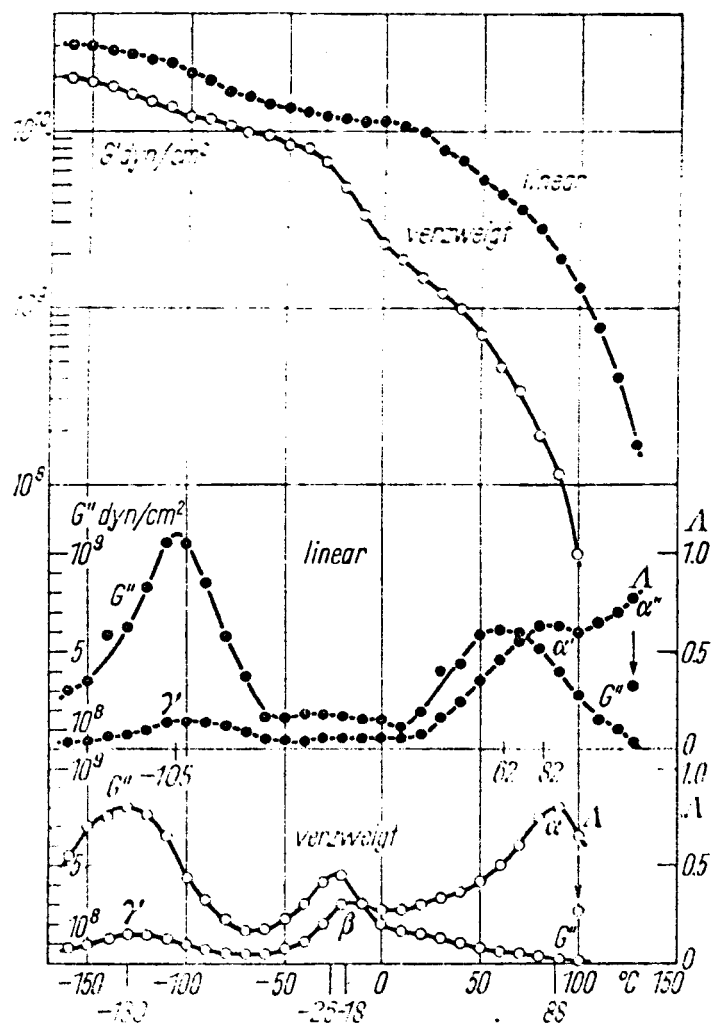


Figure 38. Temperature dependence of the real (G') and the imaginary (G'') part of the complex dynamic modulus and of the logarithmic decrement of damping (A) for linear and branched ($3\text{CH}_3/100$ atoms) polyethylene. -- Torsional vibration investigations (about 15 to 0.2 cycles) according to Schmieder.

STRENGTH AND ELONGATION

It is surprising that very little information seems to have been obtained on the strength and elongation of nonmetallic materials at very low temperatures. During the author's European visit, a few scattered references were made to tensile and impact strength measurements but not to elongation. The only coordinated study⁽³⁷⁾ seems to be one by Michel Chatain under the direction of Prof. P. Dubois at the Centre d'Etude des Matieres Plastiques in Paris. In this very extensive work, some stress-strain measurements on plastics have been carried down to -195 C. Chatain divides the mechanical performance of plastics into a fragile (brittle) temperature region and two types of plastic regions (domains) and has given critical constants for a number of polymers (Figure 39).

Since Chatain's thesis is not generally available, a number of his tensile stress-strain and breaking strength versus temperature diagrams are included here in Figures 40-59. In general, tensile modulus and tensile strength increase as the temperature decreases (PVA is an exception). For some materials (see Figure 44) only the tensile strength (not the modulus) increases. With Nylon, very high tensile strengths are attained at low temperatures but the elongation to failure is quite small. On the other hand, at low temperatures Teflon has relatively lower breaking strengths but surprisingly high elongation to failure. Careful observation of Figures 40-59 will also reveal other, more subtle differences too detailed to discuss here. An additional curve of tensile modulus versus temperature for Teflon is plotted in Figure 60. This curve reveals several transition temperatures which should be compared to transition temperatures established for Teflon by other means.

In summary, the data from Chatain provides information of considerable theoretical interest and reference should be made to his thesis for details. Moreover, the information is considered to have considerable engineering usefulness.

(37) "Contribution à l'étude des états structuraux des hauts polymères à partir de la détermination de la contrainte au seuil d'écoulement en traction", (Contribution to the Study of Structural States in High Polymers to set forth the determination of Stress to the Point of Flow in Tension), M. Chatain, a doctoral thesis at the U. of Paris (1963).

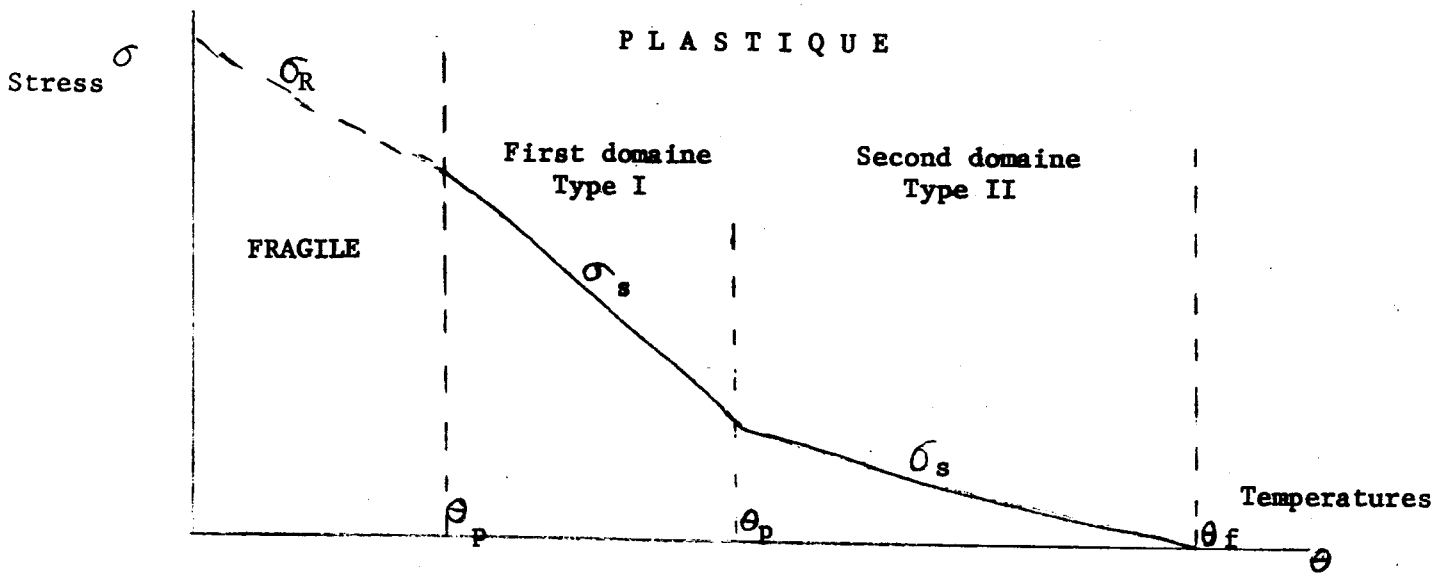


Figure 39. Different material studies have permitted the determination of the following critical temperatures (see above)

Polymer	$\theta_p (^{\circ}\text{C})$	$\theta_p (^{\circ}\text{C})$	$\theta_f (^{\circ}\text{C})$	Observations
POLYOLEFINS				
Low density polyethylene	-110, -97	+10	+100	
High density polyethylene	-21, +5	+60	+125	
Polypropylene	-20, -1	+60	+150	
POLYAMIDES				
Polyhexamethylene-adipamide	-73, -66	51 40 28	250 250 250	Desiccated sample 48 hrs. at 65% RH 3 weeks at 65% RH
Polyamide 6	0, +18	46	215	- - - - -
Polyamide 6/10	-32	50	228	There seems to be a critical temperature at +20 C
Polyamide 11		50	175	- - - - -
POLYTETRAFLUORO-ETHYLENE	-100, -82	+28	>300	There seems to be a critical tempera- ture in the neighbor- hood of 160 C
VULCANIZED RUBBER	-88 -72 -78	-57 -55 -55	-52.5 -50 -50	Under-vulcanization Optimum-vulcanization Over-vulcanization

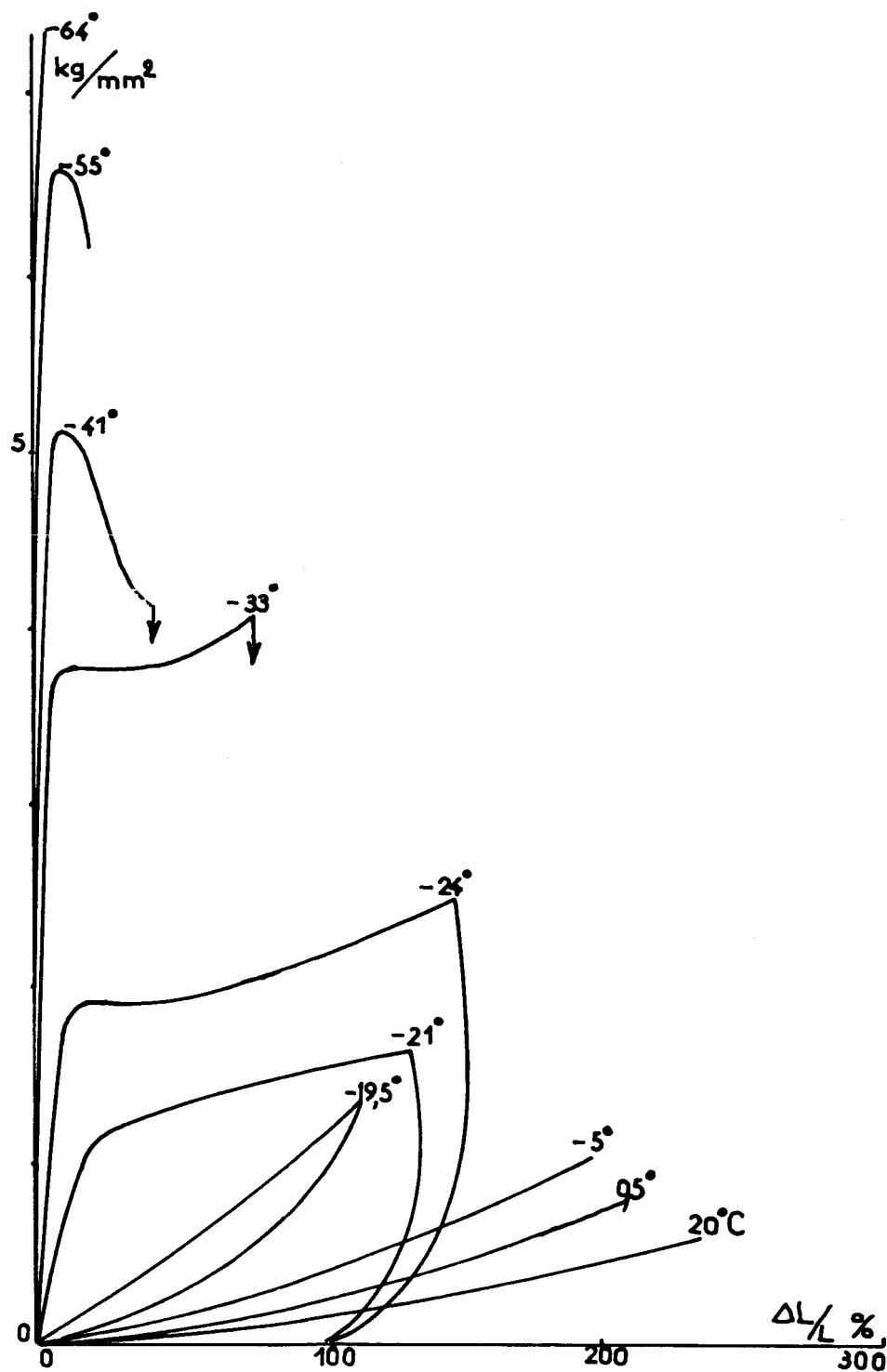


Figure 40. Stress-strain Relationship for Viton - a co-polymer of fluorinated vinylidene and hexafluoropropylene.

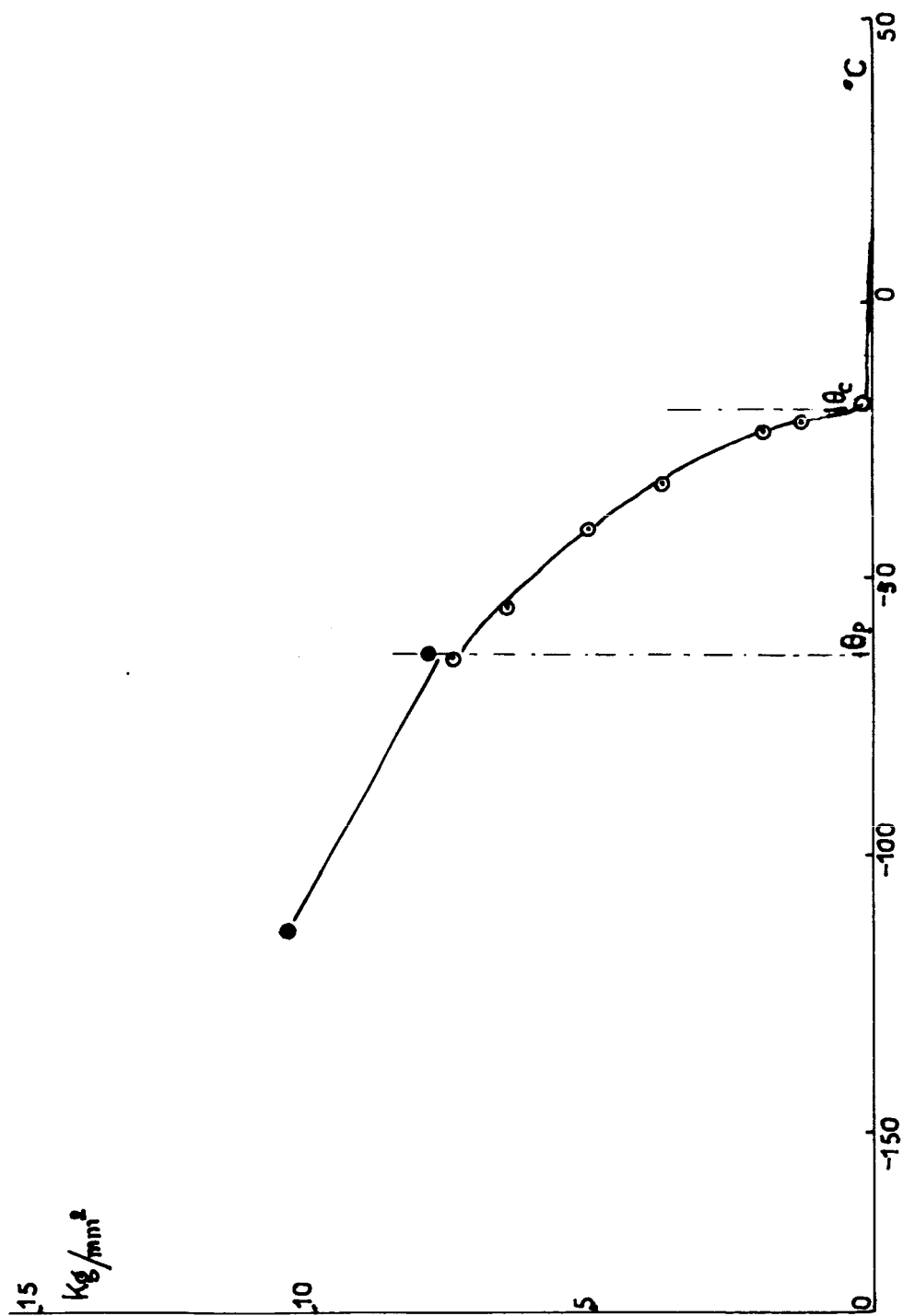


Figure 41. Tensile Strength versus Temperature for Viton

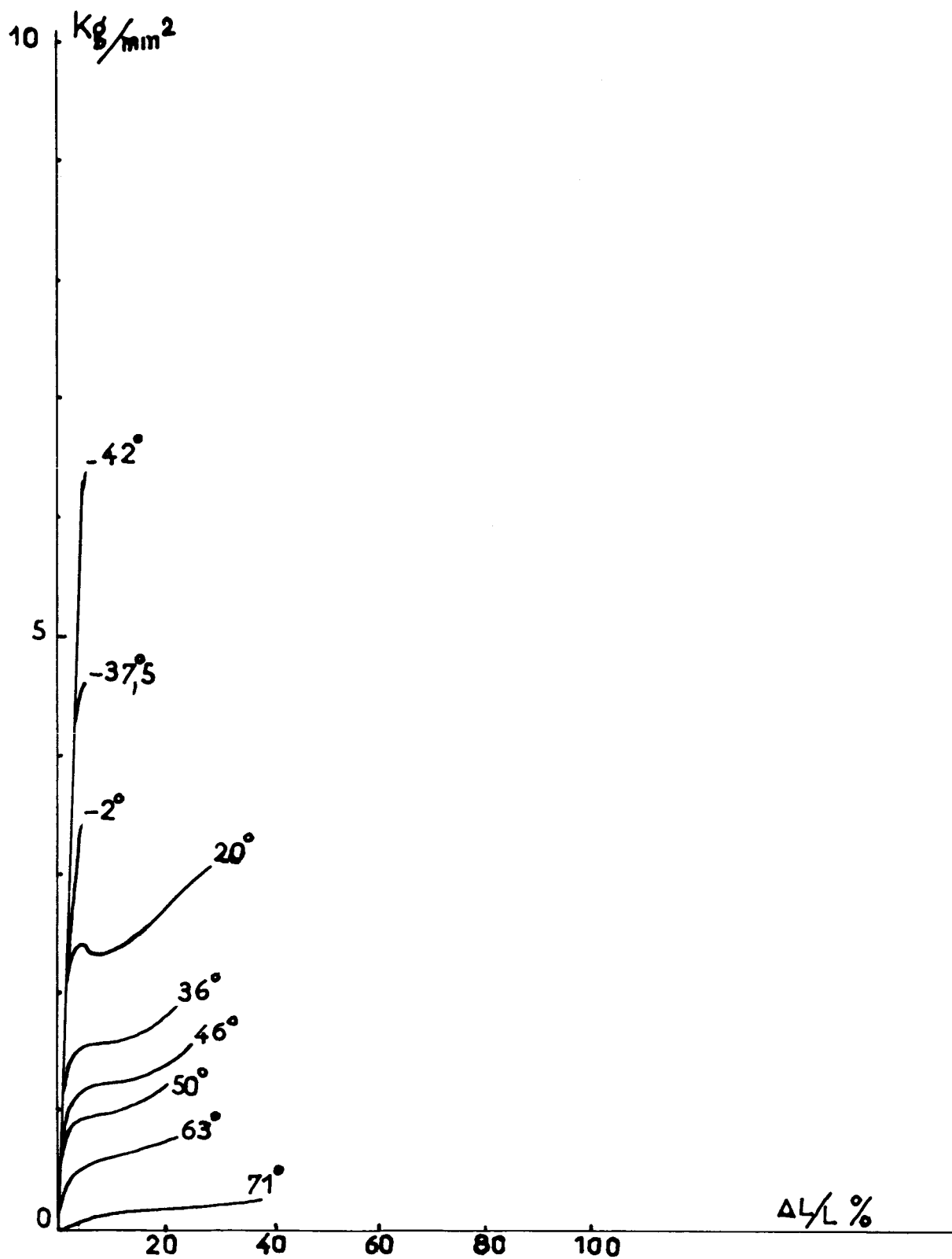


Figure 42. Stress-Strain Relationship for Cellulose Acetate

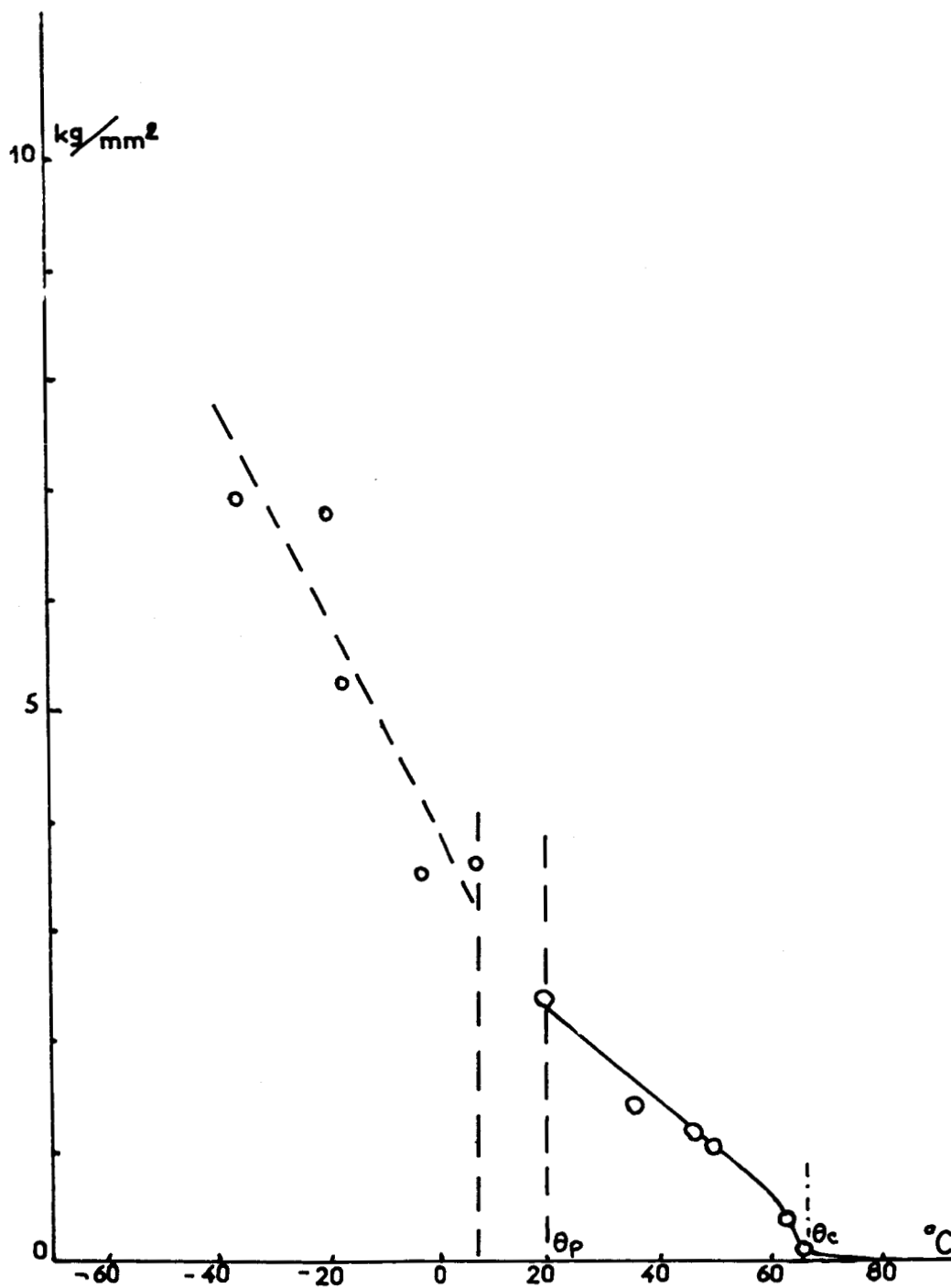


Figure 43. Tensile Strength versus Temperature for Cellulose Acetate

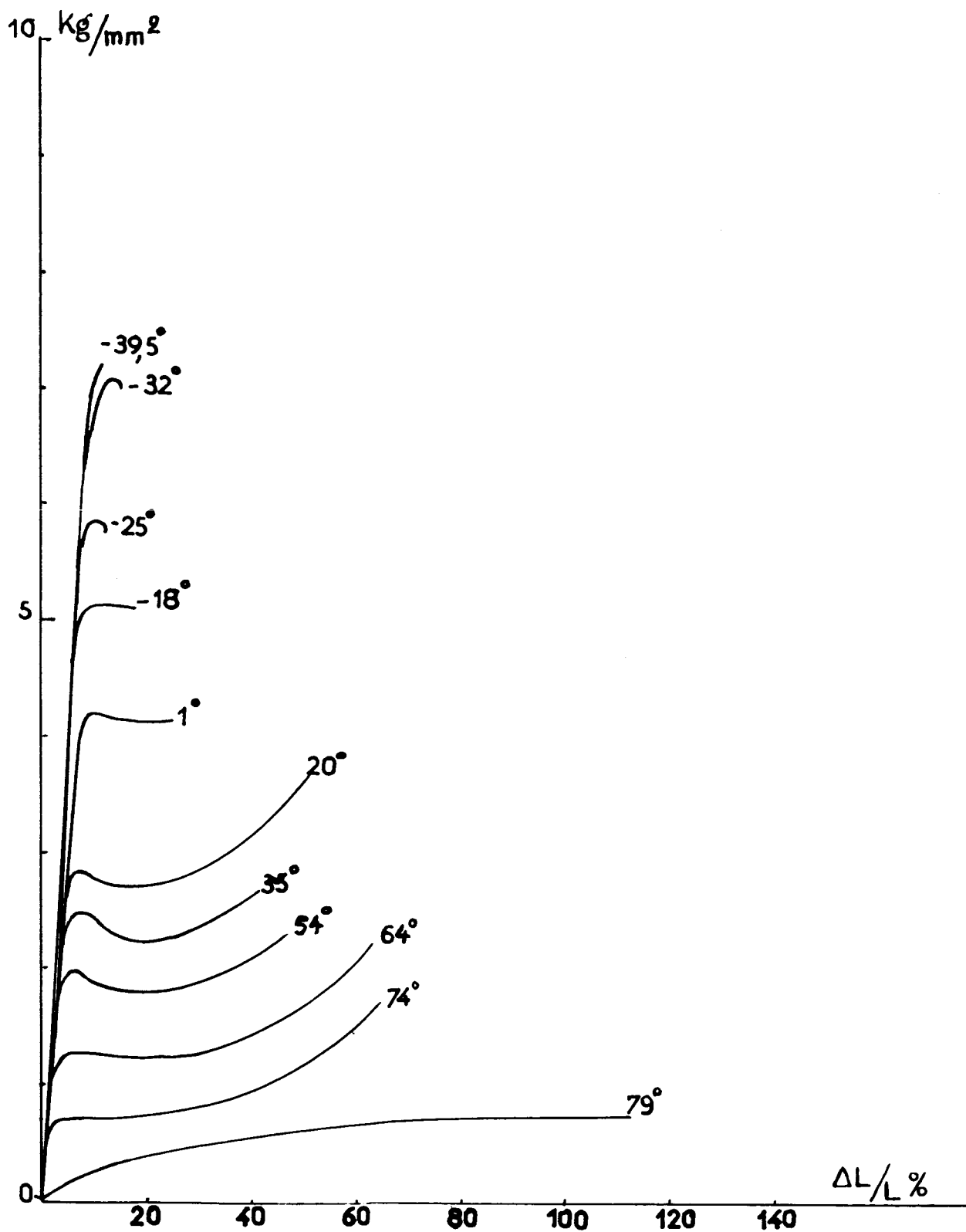


Figure 44. Stress-Strain Relationship for Cellulose Aceto-butyrate

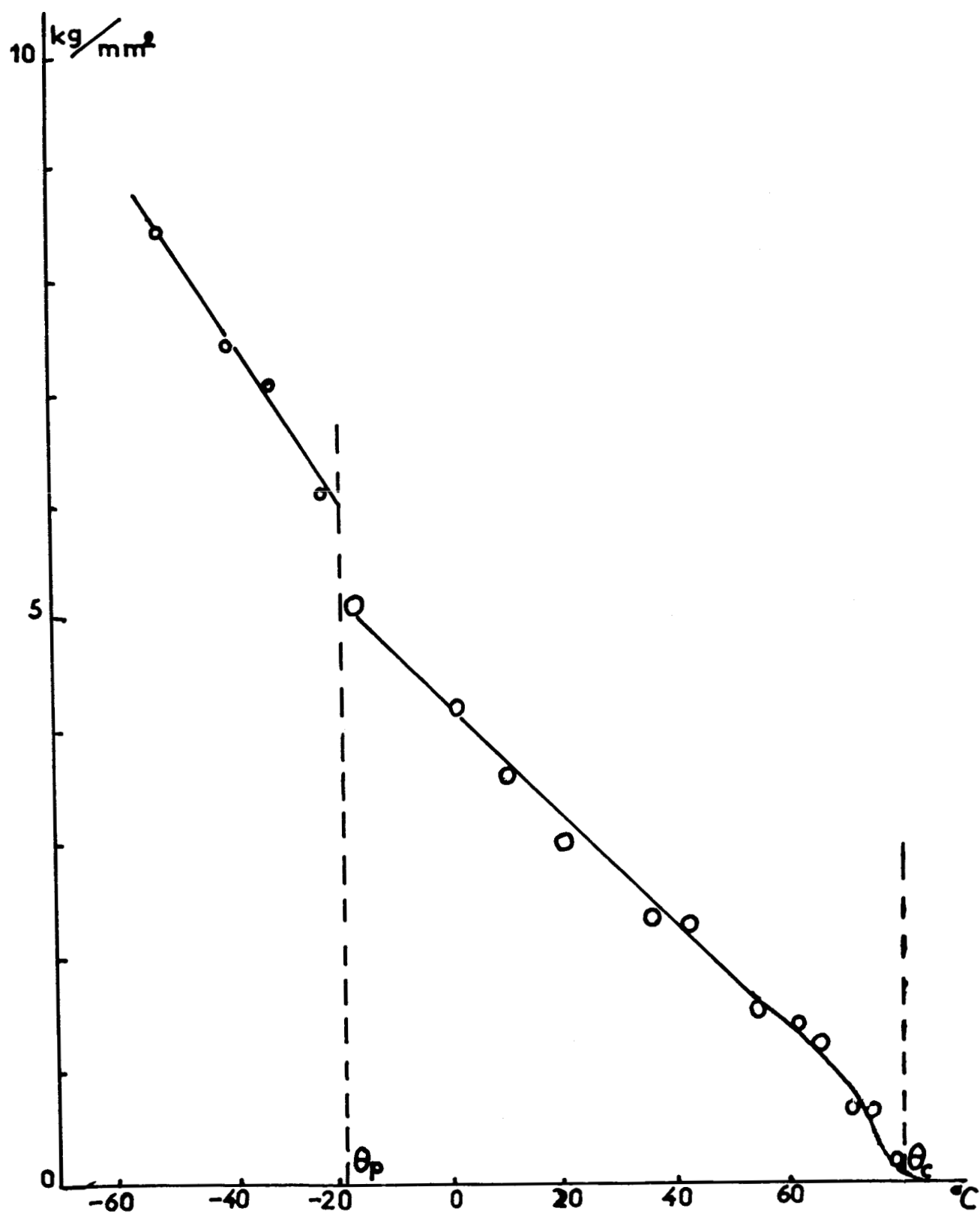


Figure 45. Tensile Strength vs. Temperature for Cellulose Aceto-butyrate

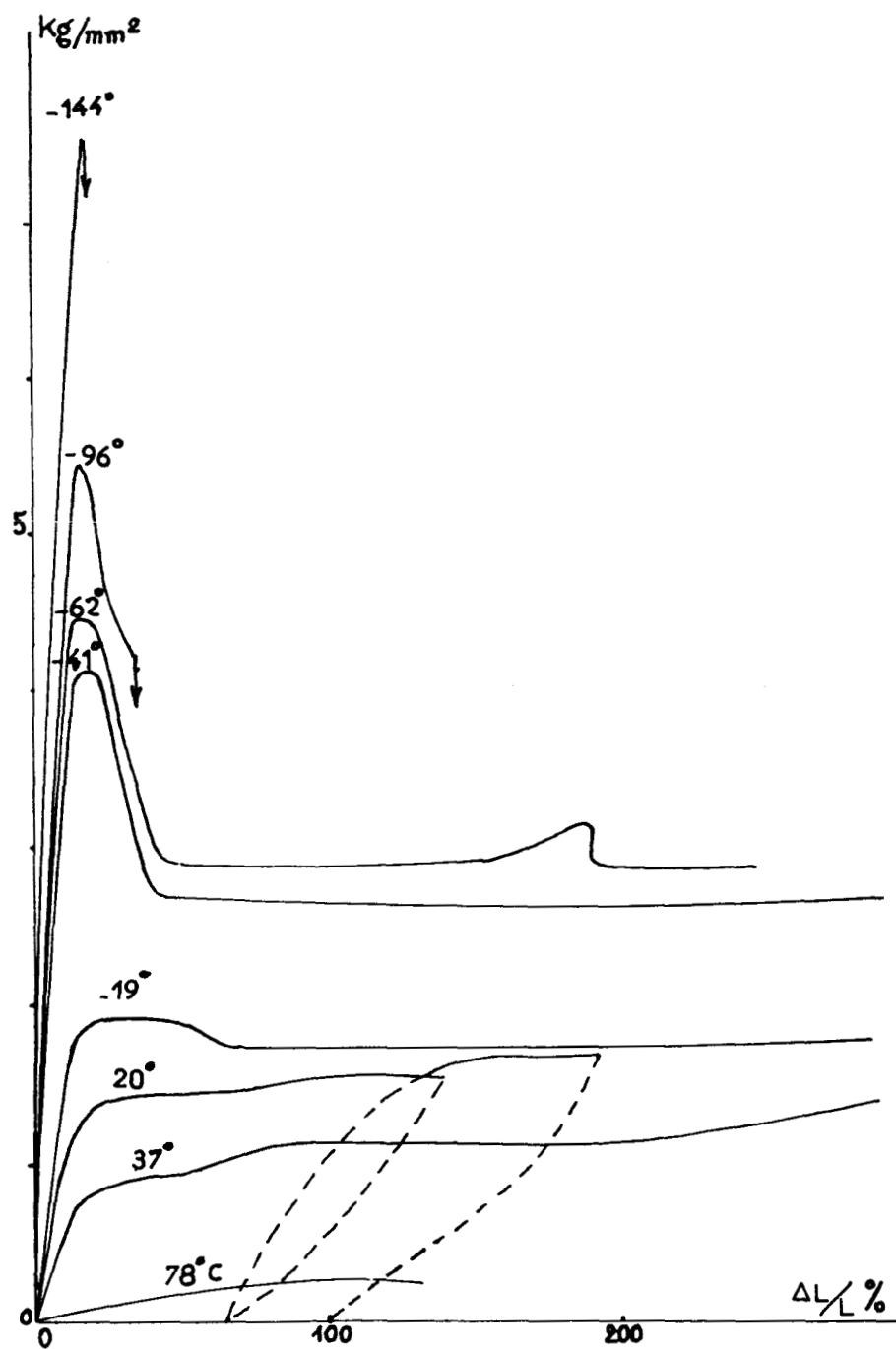


Figure 46. Stress-Strain Relationships for Low Density Polyethylene

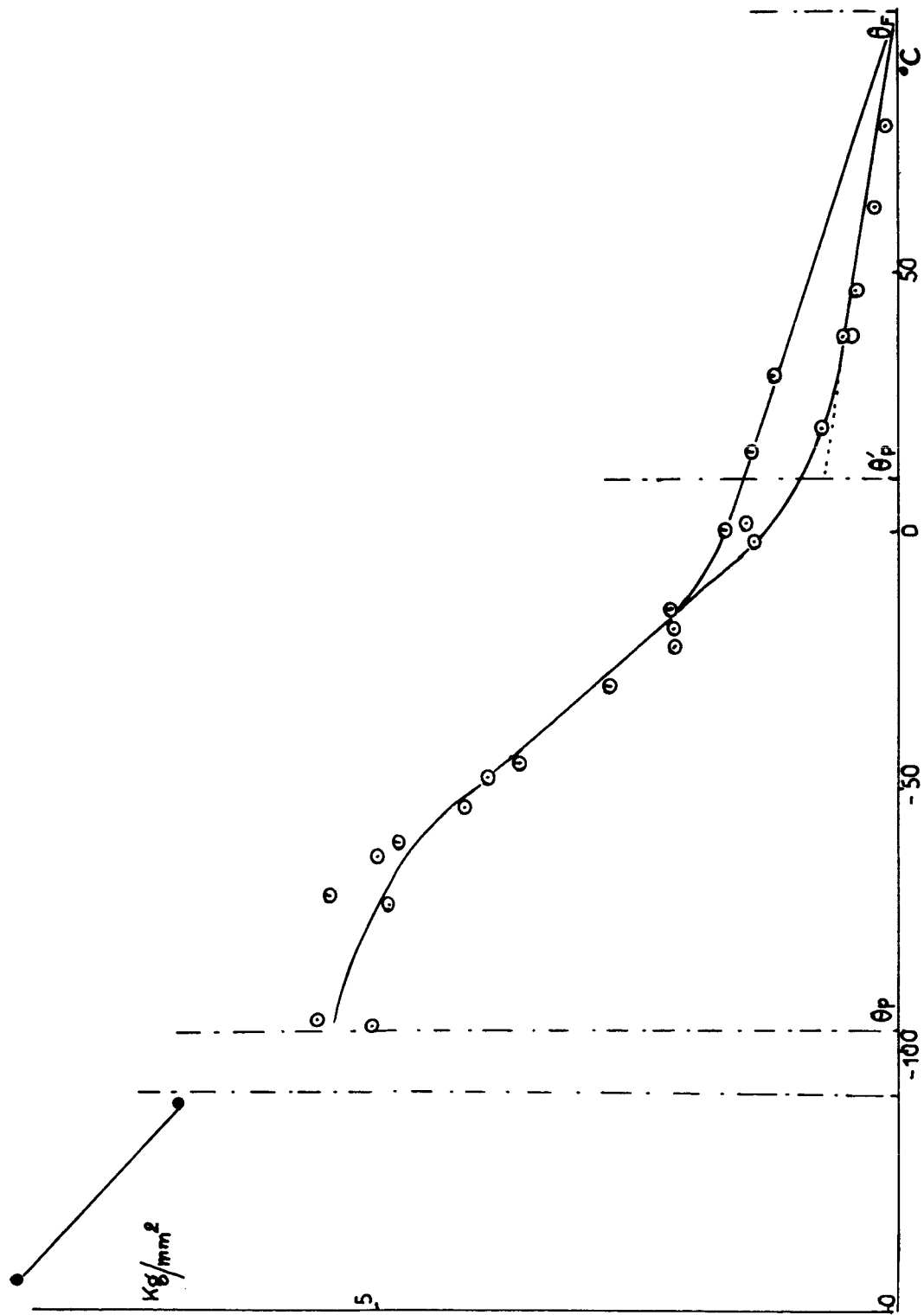


Figure 47. Tensile Strength vs. Temperature for Low Density Polyethylene

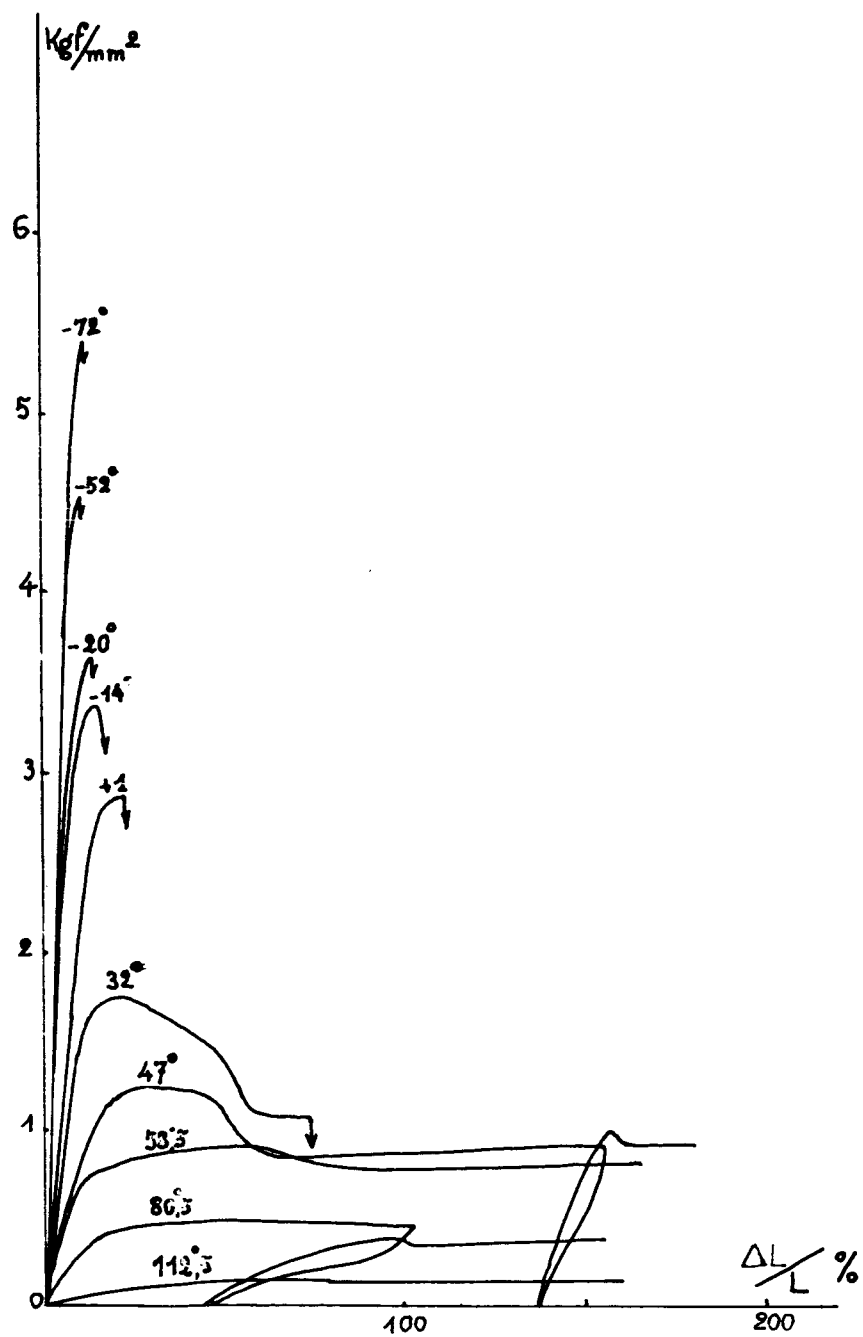


Figure 48. Stress-Strain Relationships for High Density Polyethylene

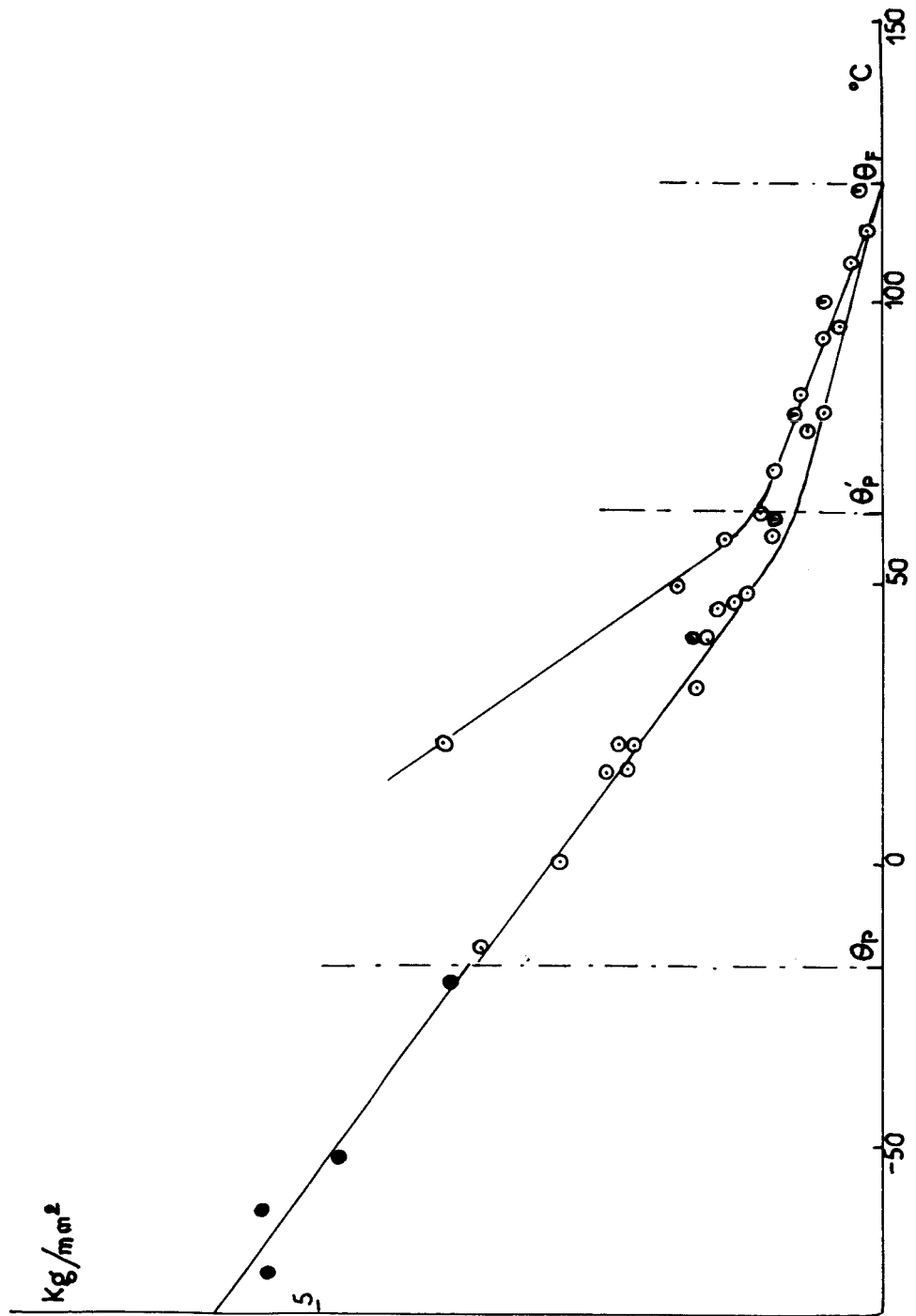


Figure 49. Tensile Strength vs. Temperature for High Density Polyethylene

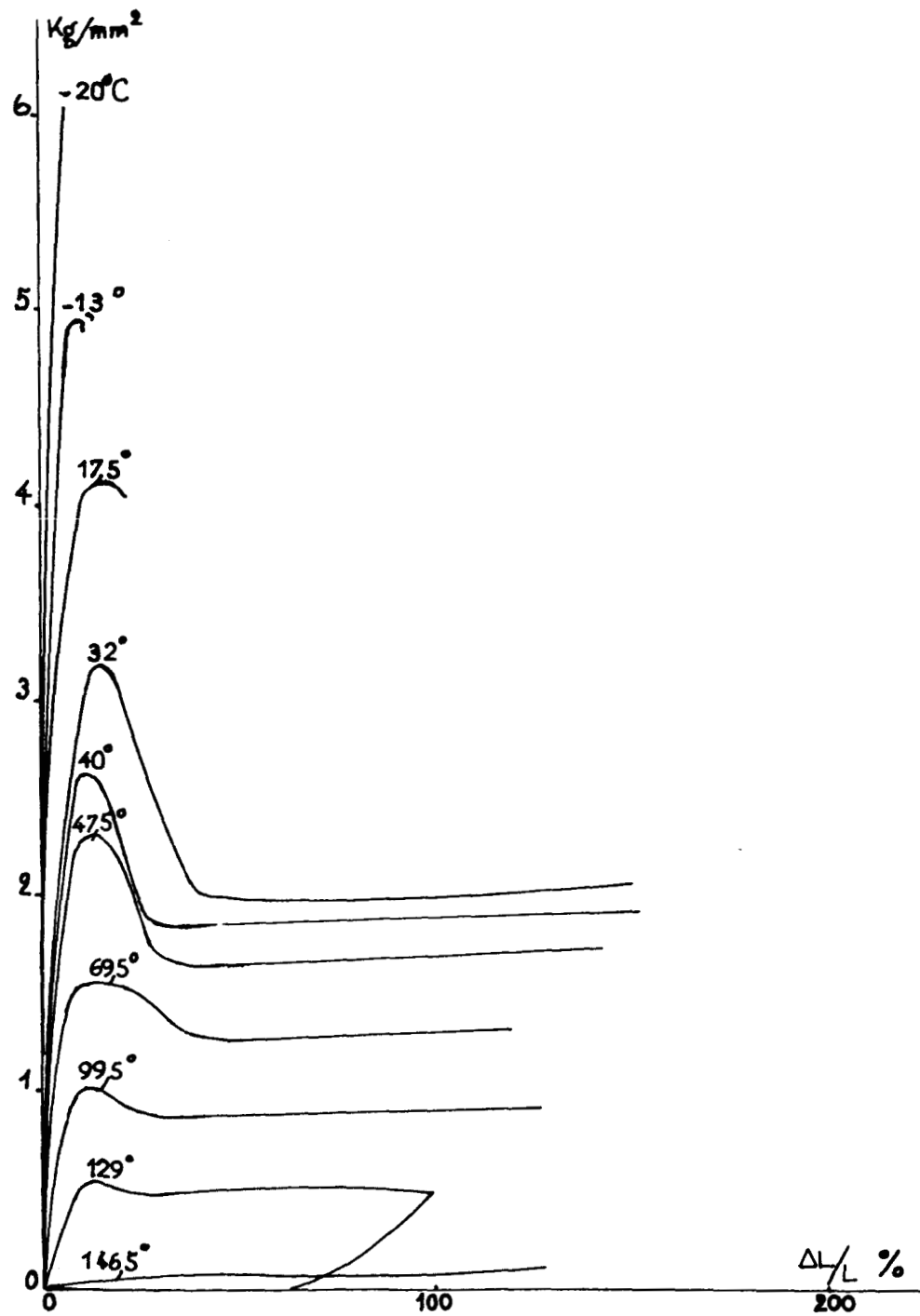


Figure 50. Stress-Strain Relationships for Polypropylene

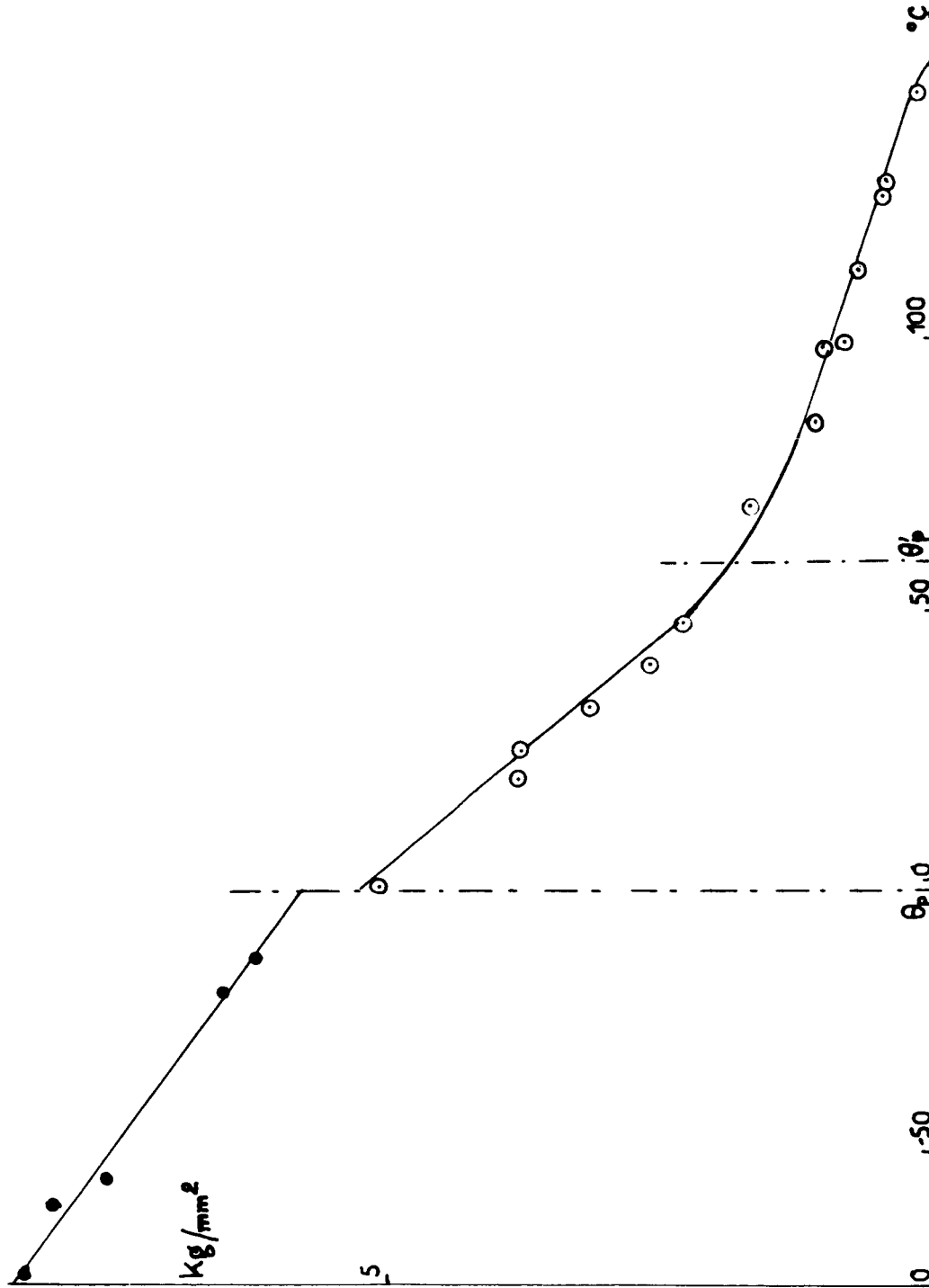


Figure 51. Tensile Strength vs. Temperature for Polypropylene

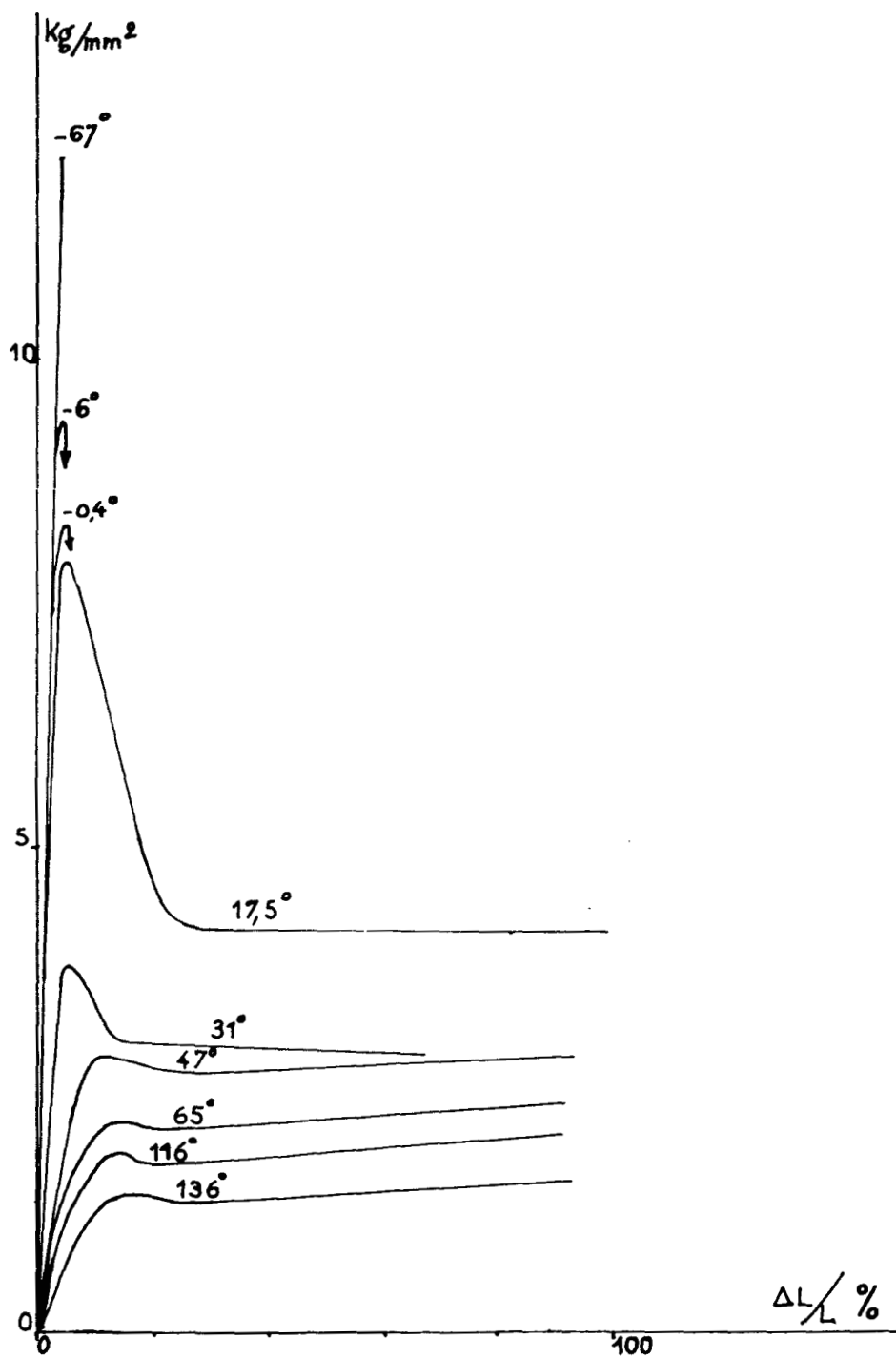


Figure 52. Stress-Strain Relationships for Polyamide (Nylon) 6

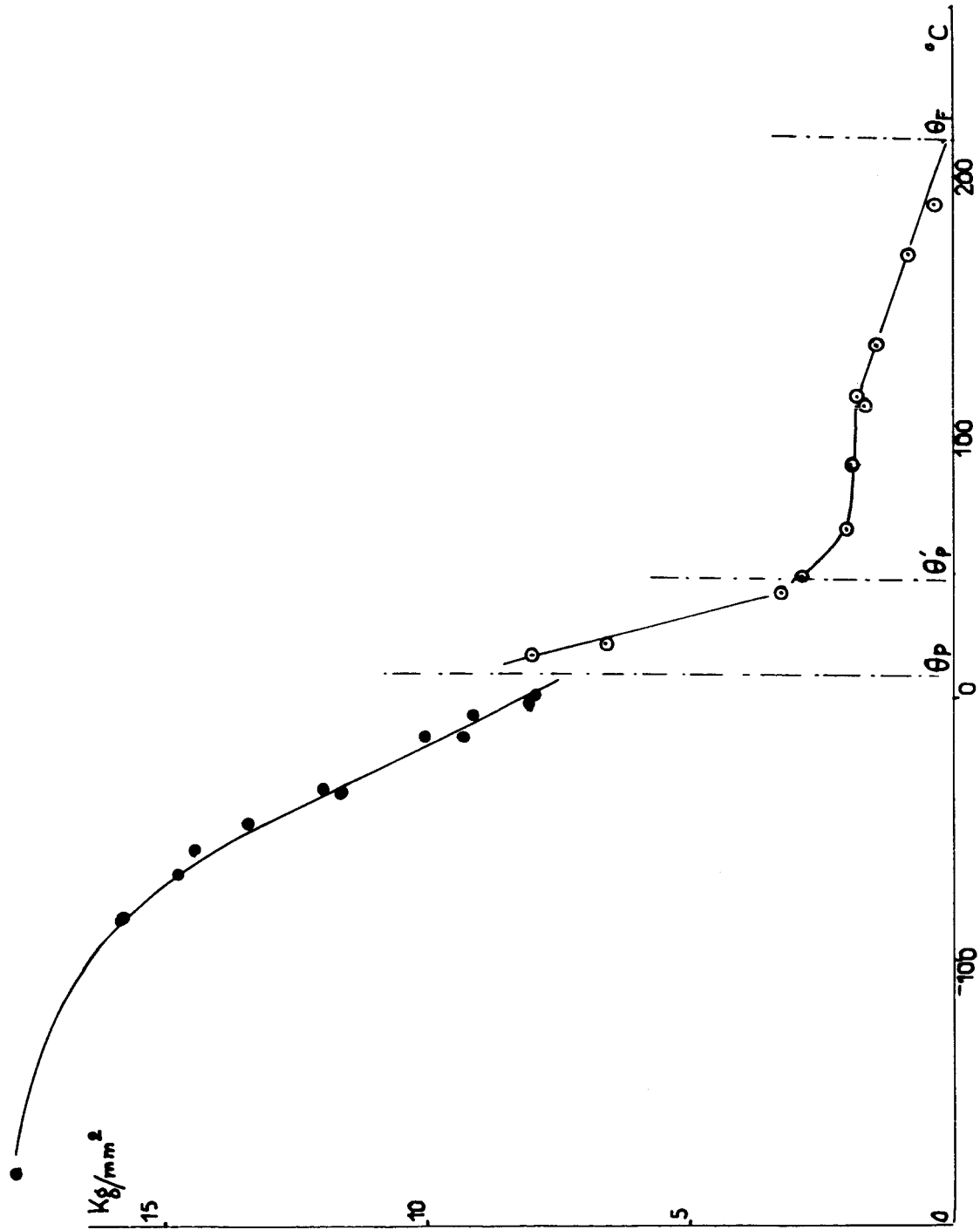


Figure 53. Tensile Strength vs. Temperature for Polyamide (Nylon) 6

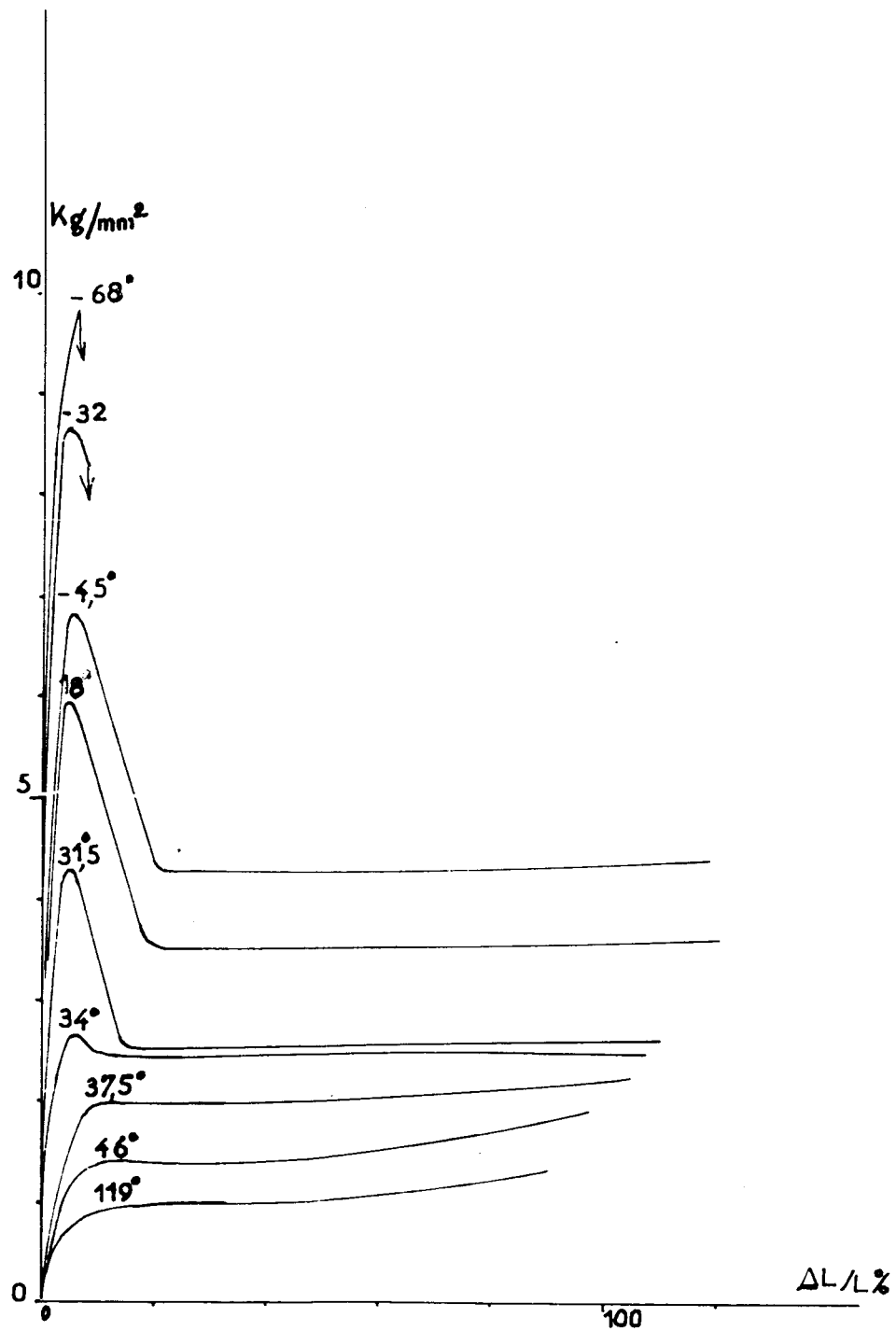


Figure 54. Stress-Strain Relationships for Polyamide (Nylon) 6/10

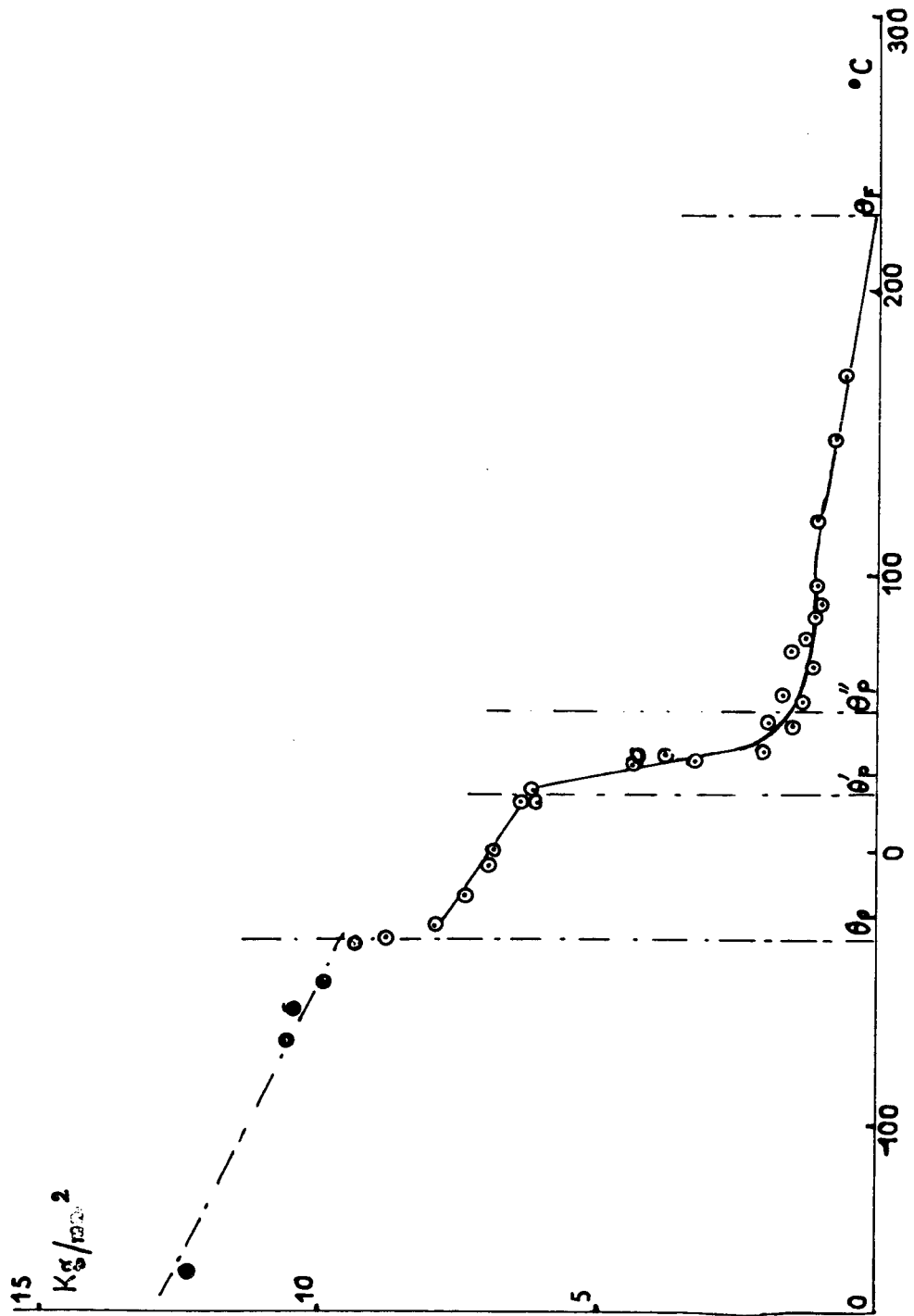


Figure 55. Tensile Strength vs. Temperature for Polyamide (Nylon) 6/10

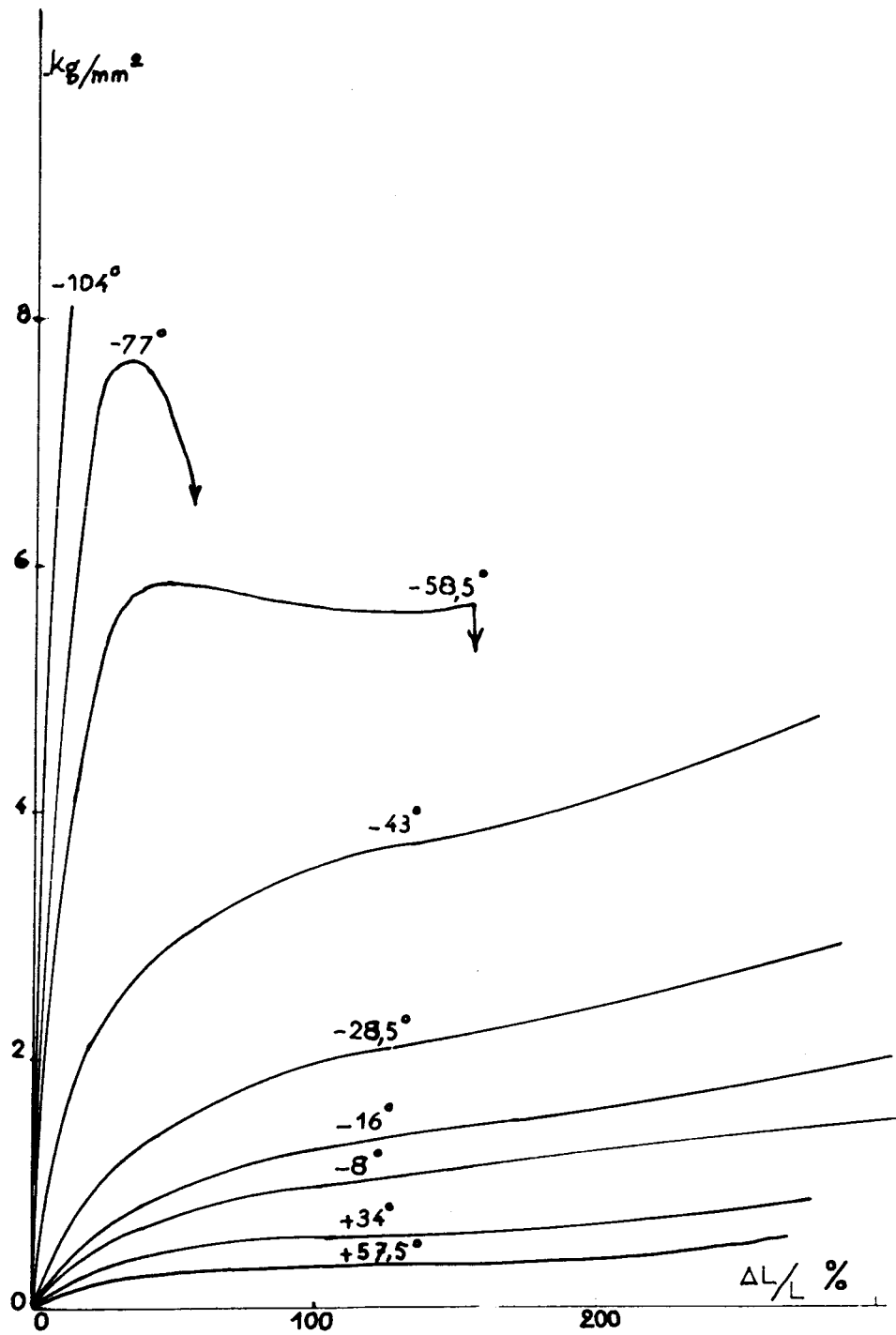


Figure 56. Stress-Strain Relationships for Polyvinylalcohol

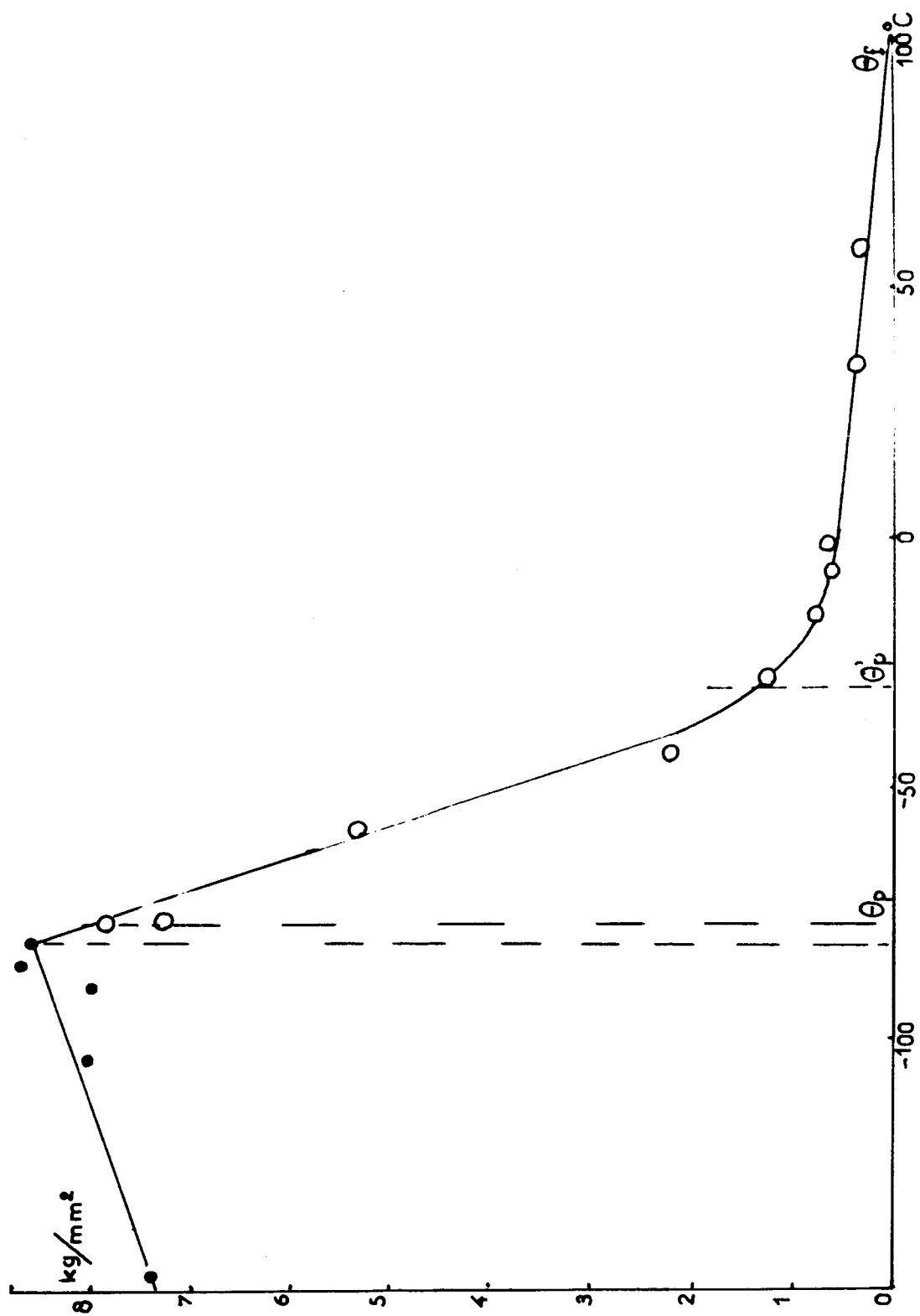


Figure 57. Tensile Strength vs. Temperature for Polyvinylalcohol

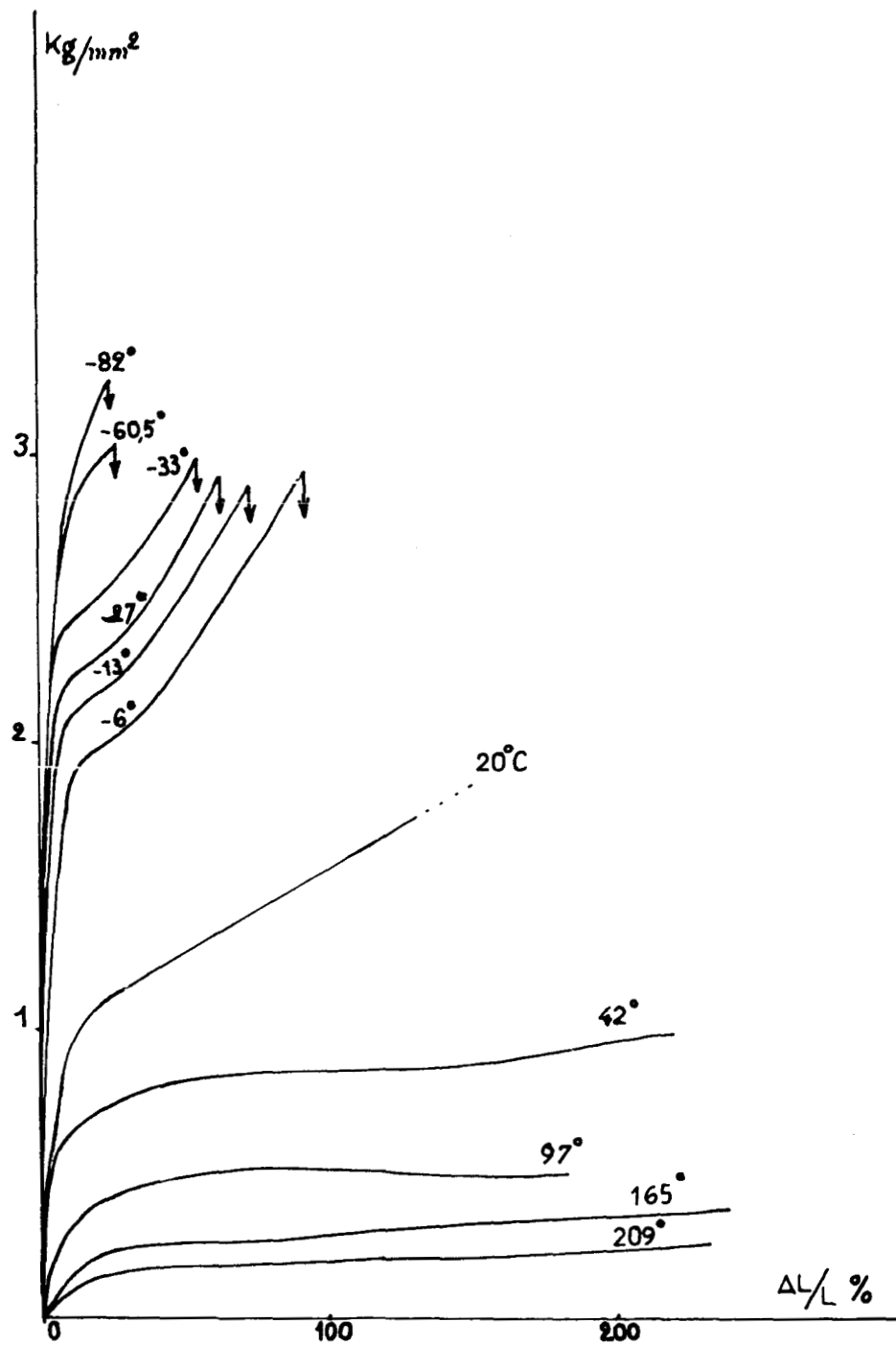


Figure 58. Stress-Strain Relationships for Polytetrafluoroethylene (Teflon)

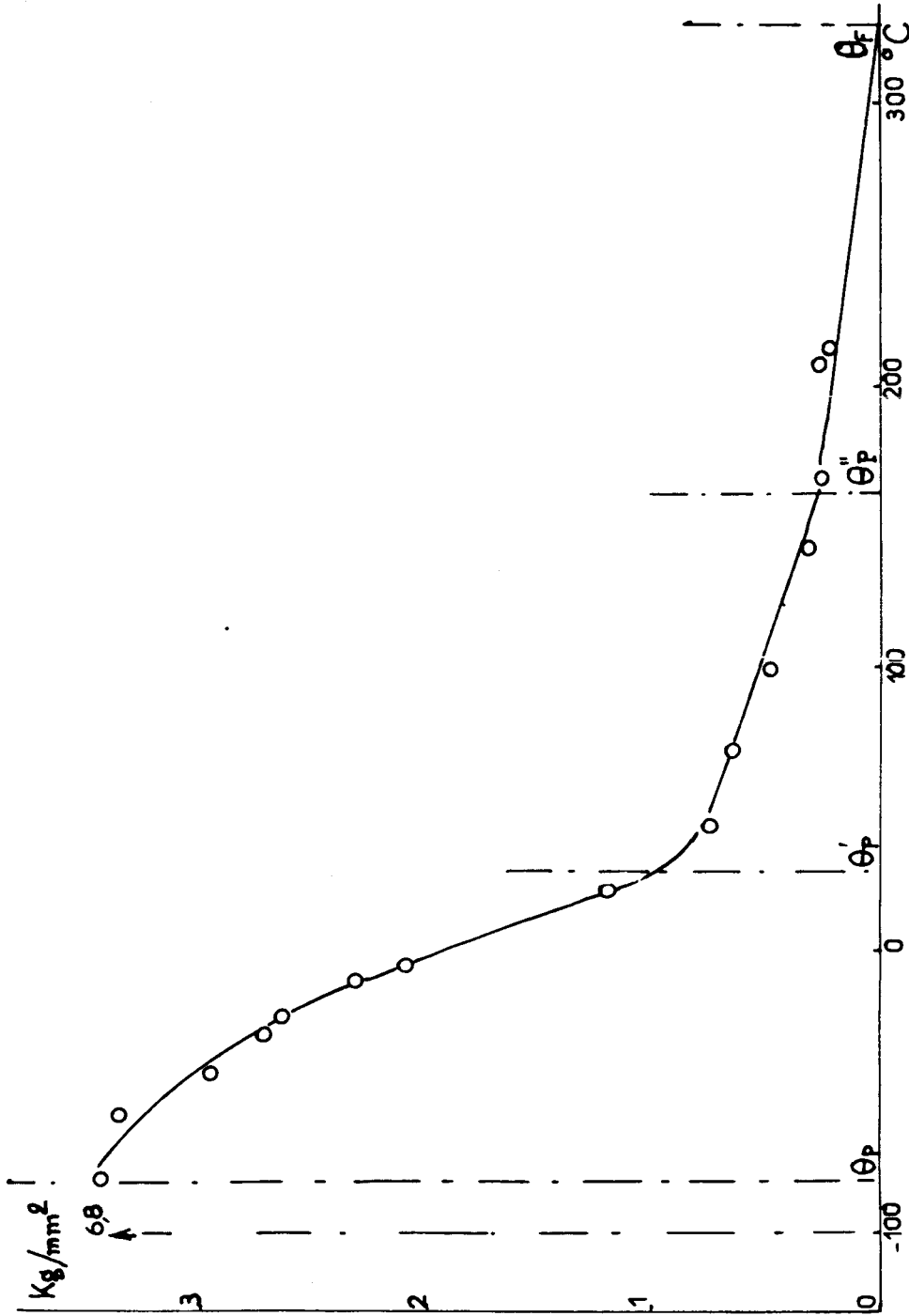


Figure 59. Tensile Strength vs. Temperature for Polytetrafluoroethylene (Teflon)

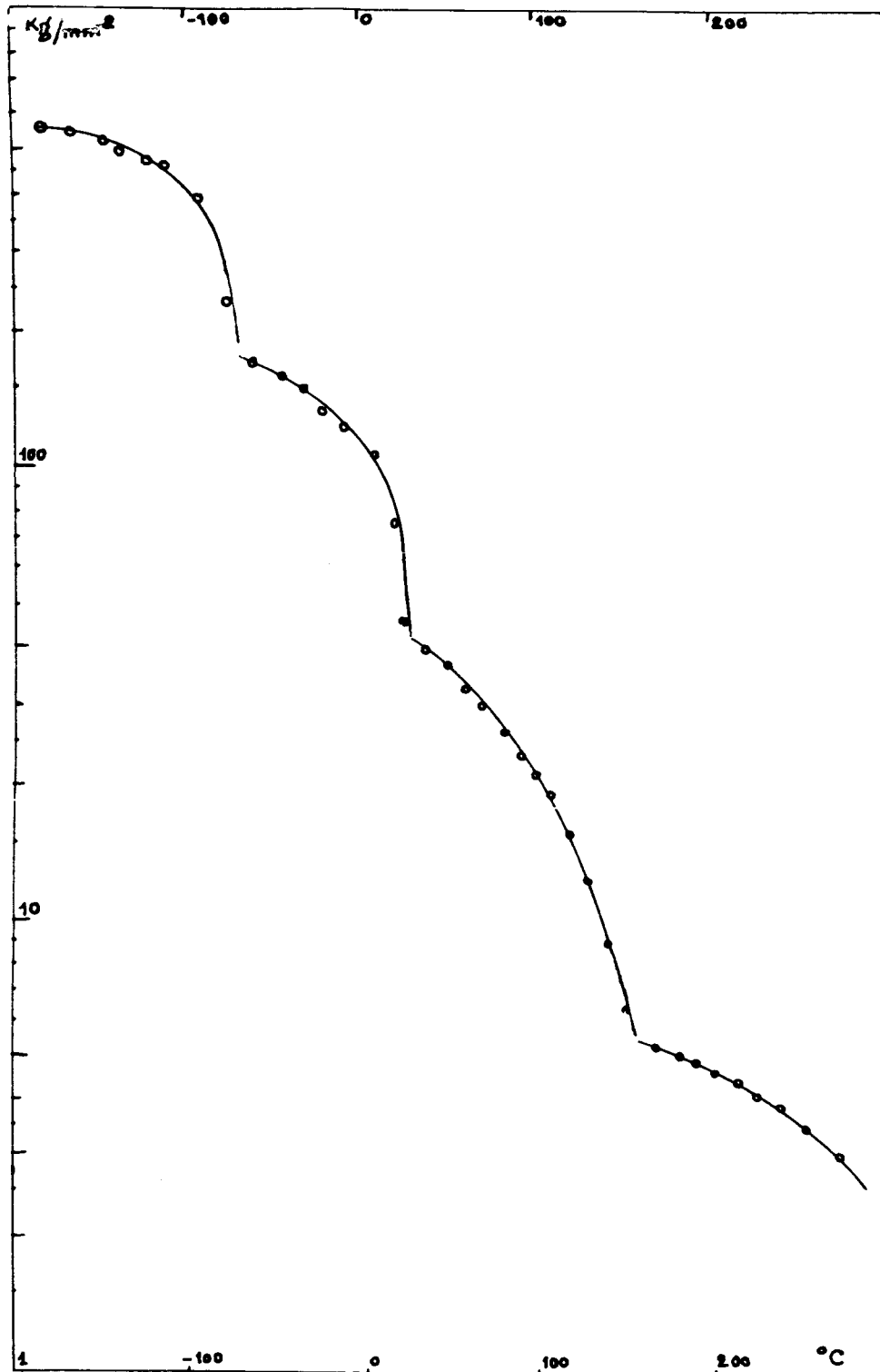


Figure 60. Tensile Modulus vs. Temperature for Polytetrafluoroethylene (Teflon)

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